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Chemical Analysis of Luminescence# 107. EXCITATION AND RECORDING OF RADIANCE DURING THE QUALITATIVE AND QUANTITATIVE CHEMICAL ANALYSIS OF LUMINESCENCE

EXCITATION OF LUMINESCENCE. The photo-excitation can be effected by any of the three methods indicated in Fig 202. From the emission spectrum of the source (1), through a filter (2), a narrow spectrum band has been serrated which then, by means of a condenser (3), will be focused on the investigated object (5). The recording part plus setup can be performed in many different ways.

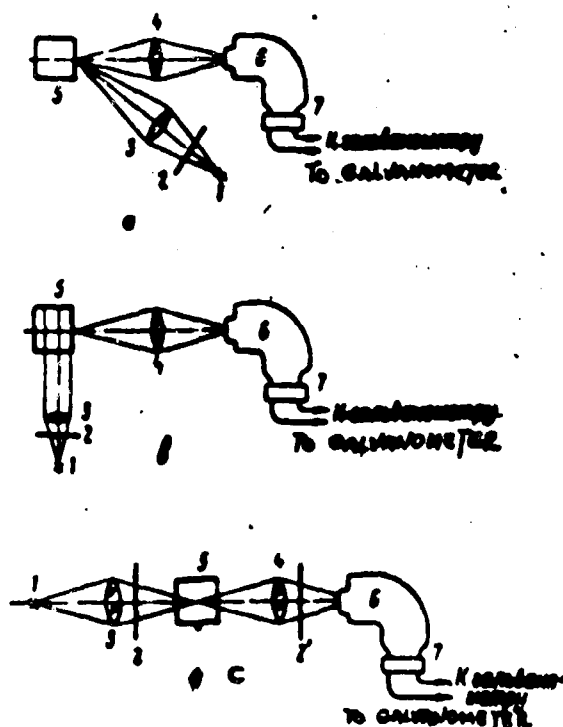


Fig. 202. Three possible ways of exciting the luminescence: a- front excitation; b- side excitation; c- through excitation; 1- lighting source; 2,2'- crossed light-filters; 3,4- condensers; 5- object to be investigated; 6- monochromator; 7- receiver of emission.

For a qualitative analysis, quite often a visual observation of the radiance is all that is required. To meter the integral intensity of the radiance, photometers are being used into whose opening the luminescence will be focused by a condenser (4). In those cases when it is necessary to determine the energy distribution in the spectrum of luminescence, a spectrophotometric device (6) is used instead of a photometer. Here, either the watcher's eye (a visual method) or a photo-film, photo-element, photo-amplifier, etc. (an objective method) can serve as the receiver of emissions (7).

Regardless of the method of the experiment applied rays of the exciting light can enter the receiver together with the luminescence. The most drastic errors may occur when the radiance to be metered has a low intensity, and the receiver is very sensitive in the frequency range of the exciting light.

To prevent the above, a method of crossed filters is being applied. Immediately after the source (1), a filter (2) is mounted which will absorb the visible part of the spectrum, and will let through the

ultra violet emission. A second filter, (2') mounted after the

analyzed object (5), will let through the luminescence light but will completely absorb the exciting rays.

In those cases when it is necessary to determine the shape of the luminescence spectrum, the method of crossed filters can be used only with a certain reservation. It is hard to select such a light-filter (2') which would fully absorb the light of luminescence. In practice, this filter will always, to a certain degree absorb the emitted radiance (and not evenly as per its spectrum) thus distorting the shape of the luminescence spectrum itself.

The most often used method of excitation is shown in Fig. 202,A. Here, the rays of the exciting light are directed at an angle of  $30^{\circ}$  -  $45^{\circ}$  to the specimen surface. The watching is done at  $90^{\circ}$  to its surface. With such arrangement of apparatus, only a negligible part of the exciting light rays dissipated by the vessel walls and the surface of the object itself, will enter the receiver. The above setup has no particular advantage in those cases when the investigated object is avidly absorbing the rays of the exciting light. They are only slightly penetrating the object mass, and the receiver will record the actual radiance emitted by the specimen surface. At the same time, the influence of the luminescence secondary absorption (see below) is reduced to a minimum.

Sometimes, it is convenient to use the method shown in Fig. 202,B, where the rays of the exciting light are at  $90^{\circ}$  to the direction of observation. The above method is being applied when working with solutions which only to a very small degree are absorbing the rays of the exciting light. It is there assumed that over their entire travel through the solution, the exciting rays have a constant intensity of radiance. With such a setup, the influence of the dissipated light can be reduced to a minimum to lower the secondary absorption, the light source should be positioned in such a way that the radiance was excited along the front wall of the vessel, at  $90^{\circ}$  to the direction of watching. The above method is used when it is necessary to take into consideration the percentage of the exciting light which was absorbed by the emanating substance; likewise, the above method is suitable for metering the degree of the radiance polarization.

When metering the polarization, either a polarized or natural light is used as a source of excitation. With the former, the degree of the radiance polarization is much higher than with the latter. Formula (18.3) can be used for conversion. With the polarized light used as a source of excitation a polarization prism will be mounted after the source (1); However, the prism will reduce the intensity of the exciting light to less than one-half of the original. Consequently, the above method might be used when investigating the objects with an intensive radiance. Natural light is being used when working on weakly luminescence objects whose radiance has a considerable

degree of polarization. To determine the degree of polarization, the spectrum apparatus (6) should be replaced by the one metering the polarization. To receive the spectrum of polarization, a Quartz monochromator shall be mounted after the source (1), and the radiance excited by different wavelengths.

The method shown in Fig. 202, 3, where the source (1) of excitation, the object to be investigated (5) and the receiver (7) are all mounted on the same optical axis, is the least suitable for investigation of the luminescence, and therefore seldom used. Here, with a "through" excitation, there is a biggest chance that the exciting light will enter the receiver, and very crossed filters will be required to stop it. Moreover, in such a case the influence of the secondary absorption (see below) can be particularly high. This method is used when investigating a lengthy radiance (phosphorence). After the excitation has been already stopped, and no exciting light can enter the receiver.

For other types of excitation (the cathode X-ray, radioactive, etc. emissions), different other sources of excitation are being used, but the recording part of the installation remains the same.

In the luminescence analysis, quite often one has to deal with small amounts of substances, many of them with a weak radiance. In result, the luminescence intensity of the specimen under investigation can turn out to be very small, indeed, and its measuring - very difficult. Thus, it is very important to select the most favorable conditions for the experiment.

Beside being characteristic to the substance itself, the intensity of the radiance depends primarily on the intensity of the exciting light; usually, this intensity is being determined by the amount of absorbed energy of the exciting source radiance. Therefore, for exciting an intensive radiance, critical is not the magnitude of the source integral brightness, but its brightness in the absorbed spectral zone. Considering that different sources have a different distribution of energy along their respective spectrum. When selecting a source one should establish how high is its radiance in the spectrum interval to be used. Usually, the most advantageous is the spectral sector close to the maximum of the substance absorption spectrum; then, in the scheme shown in Fig. 202, A, the distortion of the luminescence spectrum due to its secondary absorption (see below) will be at its minimum, and the schemes, 202, B and C, - the radiance intensity at its maximum.

To find the most absorbable sector of the spectrum, it is sometimes enough to use a qualitative estimate by watching how deep the exciting rays of the various wave-lengths are penetrating a vessel filled with the solution. Such an estimate can be performed easily as, on its path of distribution, the exciting light leaves a distinct, radiant track; The stronger the absorption, the shorter will be the track.

When selecting the wave-length of the exciting light, one should keep in mind that, according to Vavilov's Law, the quantum output of the luminescence is sufficiently high only in the stokes' part of the spectrum, and in the anti-stokes' part it drops sharply. Thus, to obtain an intensive radiance, it is vital that wave-length of the exciting light was shorter than that of the luminescence spectrum maximum. According to the stokes-Lommel Law, the above condition is automatically satisfied if the wave-lengths used for the excitation are within the maximum zone of the absorption spectrum.

THE SECONDARY ABSORPTION. When, carrying out the analysis, one should take into account that the shape of the specimen luminescence spectrum can be highly distorted by the secondary absorption of the luminescence light. Due to the fact that the spectra of absorption and luminescence superimpose each other (Fig. 187), coming out of the solution depth the luminescence light will be partly absorbed by the molecules of the radiating substance themselves. This secondary absorption (the "re-absorption") is the more intensive the more accurate is the superimposition of the spectra, the longer the path of the luminescence light in the substance, and the higher the latter's concentration. The secondary absorption takes place only in the zone where the spectra are superimposing each other; thus, the short-wave part of the spectrum will be weakened by the secondary absorption whereas the long-wave zone will remain unchanged.

Thin layers of diluted solution are used in order to reduce the secondary absorption as much as possible. However, due to a weak radiance, such conditions are often hard to create, and one has to deal with heavy layers of the luminescence spectra should be corrected to include the secondary absorption, and thus will require time-consuming calculations, the information on the absorption spectrum of the investigated substance, as well as on the distribution of the energy in the spectrum of the source of excitation. To simplify the calculations, it is desirable to carry out the experiment in such a way that the rays of the exciting light are fully absorbed the investigated specimen.

When the excitation is performed with a continuous spectrum, the actual intensity of the luminescence " $I_{act}$ " in the frequency " $\nu$ ", can be estimated in approximation from the following formula, when the observed intensity " $I_{\infty}$ " of luminescence is known:

$$I_{\text{act}} = I_{\text{exc}} \frac{\int_0^\pi I_r \frac{\cos \varphi}{a_n} d\varphi}{\int_0^\pi I_r \frac{\cos \varphi}{a_n + a_n \cos \varphi} d\varphi} \quad (20.1)$$

where:  $a_n$  and  $a_n$  - coefficients of absorption of the luminescence and the exciting light rays, respectively;

$I_r$  - function of the energy distribution in the spectrum of the exciting source;

$\varphi$  - the refraction angle of the exciting light in the investigated specimen.

The calculation will be considerably simplified if a monochromatic emission is used for the excitation (only a single line is separated from the exciting spectrum). The formula (20.1) will look as follows:

$$I_{\text{act}} = I_{\text{exc}} \frac{a_n + a_n \cos \varphi}{a_n} \quad (20.2)$$

However, neither of the (20.1) and (20.2) formulas provides for repeated process of absorption and the resultant excitation of molecules of the luminescing substance. At the same time, during the experiment, the luminescence spectrum is a total of all radiances formed in the solution. Consequently, the values for " $I_{\text{act}}$ " calculated from formulas (20.1) and (20.2) turn out to be not very accurate.



Fig. 203. Curves showing how the secondary absorption and the secondary luminescence affect the shape of luminescence spectrum of the fluorescein solution: a - a 0.1 cm. thick layer; b - a 1 cm. thick layer; 1 - spectrum measured as is; 2 - spectrum with corrections for the secondary absorption; 3 - spectrum with corrections for the secondary luminescence.

The calculation made on the above secondary phenomena reveals that the luminescence spectrum corrected for the secondary absorption only, is somewhat shifting towards the long waves as against the actual spectrum which includes both the secondary and the subsequent radiances. Fig. 203 shows the results of calculations for the fluorescein pigment. One can see that with a thin fluorescing layer, there, is no influence of the secondary radiance (Fig. 203,a). In a heavy layer, this influence becomes more distinct (Fig. 203,b). Therefore, when working with thin layers of the luminescing diluted solutions, corrections for the secondary radiance can be ignored.

Of a great importance is also the correct selection of the solution concentration and of the luminescent layer thickness. If a specimen contains only but little of the substance, the intensity of the luminescence goes up with the concentration. However, later, a concentration - generated damping action takes place and as a result, the radiance intensity of the specimen drops drastically. At the same time, with a higher concentration, the weakening of the exciting light highly effects the depth of its penetration into the substance, and also the influence of the secondary absorption will go up sharply. The most intensive radiance is observed usually in diluted solutions whose concentration equals from  $10^{-2}$  up to  $10^{-4}$  moles/liter.

Provided the secondary absorption is either small or does not exist, and the solution concentration is low, it is advisable to work with heavy layers (up to 1 cm.) of the substance, as within certain limits, the intensity of radiance goes up with the layer thickness. However, it seems practically impossible to fully utilize the light coming from so wide light fluxes; therefore, when the readings are expected to be accurate, the radiating layer should not be heavier than 1 mm. When the concentration is intensive, the exciting light does not penetrate the solution at all, but is fully absorbed right at its very surface. In such a case, one can work with thin layers, using just a small amount of the substance to be investigated.

Recording the Luminescence. Radiance of the investigated specimen is evenly radiating in all directions (Lommel's law). To utilize the emanating light-flux as much as possible, and to direct it into the receiver, condenser lens (4) (see Fig. 200) are being applied. If a spectral device (6) has been mounted in



part of the receiver, the luminescing flux will be utilized best with its collimator completely filled with light; the above condition can be attained also by means of special illuminating circuits (see chapter 13, #45).

Serious attention should be paid to the selection of receivers which are mostly not the same extent sensitive in various parts of the spectrum. Depending on the spectral composition of the emission, one should select a receiver whose peak sensitivity would be close to the maximum of the luminescence spectrum. For example, receivers with antimony-caesium photo-cathodes should be used for recording a green, blue-violet or ultra-violet luminescence. Receivers with either multi-alkaline or oxygen-caesium photo-cathodes are being used for metering the yellow and red luminescence. Non-selective receivers the thermo-elements and bolometers are applied for recording a long-wave red and infra-red luminescence (for more details on the light receivers see chapter 11, # 45).

#### # Qualitative Analysis of Luminescence

The problems to which the luminescence analysis is being applied are extremely varied; even more varied are the substances subjected to the investigation; consequently, depending on specific properties of the object to be analyzed, different methods of analysis are being applied. However, all the variety of individual techniques can be grouped in a comparatively small number of methods of a more general nature, which are being used in a chemical analysis of luminescence concerning a widest range of substances.

#### Special Features of a Qualitative Analysis of Luminescence.

By carrying out a qualitative, chemical analysis of luminescence, we can by the radiance spectrum detect the presence of a certain substance, or a group of substances in the specimen under investigation, and also we can control the process of a chemical reaction. More often than other, the luminescence analysis is being used for research on the natural radiance of the substance. However, the problem is not so simple as only few compounds have a distinct, easily recognized spectrum of luminescence by which one can unmistakably establish the presence of a certain substance (these include: the rare-earths and the uranium compounds, porphyrines, chlorophyll and few others); However, in majority of cases, the luminescence spectra appear as wide, washed-out bands without any oscillating structure. In mixtures of two or more luminescent substances, the emission bands of individual components often superimpose one another. Thus, the luminescence analysis is easy only when either the mixture contains just a single luminescent substance or when the components have their respective radiance in different parts of the spectrum (for instance, the red and the blue radiance. However, such cases

but rarely.

Usually, prior to performing the analysis, the mixture is being subjected to a preliminary processing which consists in elimination of all hampering ingredients and separating the component of a special interest to us. There are many and varied methods leading to such a separation; various chemical reactions are here applied, heat fractionation, and also the techniques of an ordinary and the luminescent chromatography. The latter is more and more used.

The luminescent Chromatography represents a variation to an ordinary chromatographic method of separating the mixture into individual components; here, the individual zones are being detected by watching the luminescence in the separating them column. In those cases when non-luminescent substances are being chromatographed, luminescing adsorbents are used. Then, on the background of a luminescing column, dark strips will clearly appear over the zones containing the non-luminescing components of the mixture.

Equally important is the Method of Chromatographing on Paper. A drop of the solution to be investigated shall be deposited on a paper strip, close to its bottom; after it has been dried, the strip bottom end shall be immersed into a solvent for a period of 6-12 hours. The liquid will start rising up the paper strip; components contained in the drop will follow the solvent. They proceed on the paper at a different speed which, however, is always lower than that of the pure solvent.

Quantitatively, the above process is usually characterized by the following formula:

$$R_f = \frac{A_s}{A_f} \quad (20.3)$$

Where: " $A_s$ " and " $A_f$ " - distances from the place where the drop has been deposited up to the head of the travel made by the dissolves substance and the solvent itself, respectively.

The value of  $R_f$  < 1; assuming the uniform conditions of the experiment (similar kind of paper, same solvent, same temperature, etc.), the above value remains constant for each component. The chromatogram will show spots each tied to an individual component of the mixture. All of them distributed according to their respective value for " $R_f$ ". Position of these spots will be established by their characteristic fluorescence. In this way, one can detect in a specimen the existence of as little as one-hundreth of a micro-gram of the investigated substance. Sometimes, the same goal can be attained

exciting the phosphorence of the substance. For this purpose, the chromatogram should be for few seconds cooled in liquid nitrogen, and then subjected to a short excitation; the formed radiance allows establishing the zones of the substance distribution. When the investigated substances show no radiance at all, the chromatograms can be sometimes successfully processed in special solutions which make the spots luminescent.

#### Special Techniques of the Qualitative Analysis of Luminescence.

Although a mixture has been preliminarily separated, quite often special procedures are being applied which take into account the special properties of the investigated class of substances. For example, often the luminescence analysis is being carried out at a low temperature when an oscillating structure appears in the spectrum of many a compound, a feature which makes the spectrum more characteristic. The analysis of cancerogenous hydrocarbons of a high molecular weight, is being carried out in a viscous medium (in oil) where the structure of their spectra comes out more clearly, and some other hampering factors are eliminated (# 112).

E.V. Shpol'skii and his associates, and later also some other scientists have proved that many organic substances (multi-nuclear condensed hydrocarbons, aromatic aldehydes and ketones, anthraquinones, phthalocyanin and its derivatives, as well as some pigments) when frozen in the neutral, standard paraffins (pentane, heptane, hexane, etc.) will have their luminescence spectra split in groups of narrow lines, whose width will vary from 2 up to 10  $\text{cm}^{-1}$ . The appearance of these characteristic lines, permits a fast and reliable detection of extremely small amounts of the above listed substances in the specimen.

When analyzing a multi-component mixture, one should keep in mind that each of the components has its own spectrum of absorption. Therefore, it is advisable to use the excitation purpose, monochromatic rays of a different wave-length so that each of them is exciting just one of the components; this procedure will make the analysis considerably easier.

At low temperatures, besides a short-time radiance-fluorescence, the solution of many a compound has also a protracted after-radiance- phosphorence, a circumstance which is an important analytical feature of the investigated substance. In case of a B-process, the radiance spectra are clearly shifted towards the long waves in relation to the spectra of fluorescence, a feature that often helps in analysis of substances with either an ultra-violet or blue luminescence.

During a qualitative analysis of luminescence, a great help is desired also from the polarization spectra which are strongly linked to the chemical structure of the investigated substances, and in some cases, can be even more indicative

then the spectra of both absorption and luminescence of the said compounds (Fig. 204).

When carrying out a qualitative analysis of minerals, limestones, clays, ceramics, glass, optical crystals, and other substances, quite often they meter the curves of the thermic fading-out whose magnitude, position and number of maximums turn out to be sufficiently characteristic.

Despite all the above procedures, quite often the accuracy of obtained results remain doubtful. Consequently, after the analysis has been finished, the investigated object is sometimes subjected to additional experiments using, for example, the characteristic interdependence of many substances between the color of their radiance and the value of the solution "pH (Fig. 186); also, other procedures are being used. Here, when working out a technique for a luminescence analysis of a given type of compounds, one should be sure that the additional experiments and procedures are featuring a considerable sensitivity but do not consume much time.

Luminescent Reactions. Analysis reactions are widely used in the practice of chemical analysis; they allow detecting certain substances by a changed color of their solution, by the sediment formed, or by other characteristic symptoms. The luminescent reactions are one of the types of analytical reactions. They are characterized by a change in the luminescence properties of the substance; during the reaction, the luminescence spectrum of the investigated object becomes deformed, the radiance either fades away, or becomes brighter.

Luminescent reactions can be performed also on substances which have no luminescent capability. In such cases, the reaction is being conducted in such a way that, after it has been terminated, should be thoroughly studied, and the conditions in which the analysis will be carried out, should be rigidly standardized.

# 109. The Quantitative Analysis of Luminescence.  
A quantitative analysis of luminescence allows establishing the concentration of the investigated substance in the sample, by metering the brightness of its radiance; it also reveals the termination of the reaction by the luminescence having

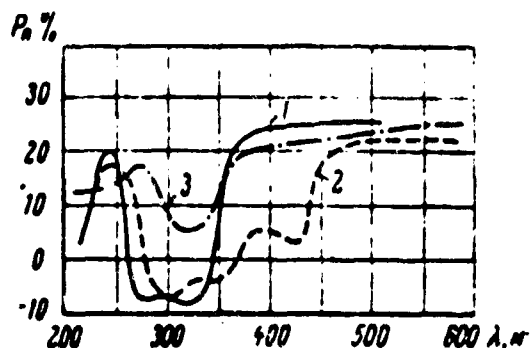


Fig. 204. polarization spectra of the glycerine solutions of pigments:  
1- Fluorescein;  
2- Rhodamine S;  
3- Acridine orange pigment;  
Long waves of the exciting light are plotted on the abscissa axis.

appeared. It should be pointed out that the main difference between a qualitative and a quantitative analysis of luminescence consists in the fact that the features just detected by a qualitative analysis, in a quantitative analysis are measured and processed with all necessary corrections considered.

Quantitative Analysis of Luminescence Based on the Radiance Brightness. All methods concerning this type of analysis are based on a certain definite interdependence between the brightness of the radiance and the substance concentration in the sample. One should try to carry out the analysis in conditions providing a straight proportion between these two factors. Here, the concentration of the investigated substance can be determined by directly comparing the radiance intensity of the analyzed specimen with that of a standard one. When the concentration is considerable, over  $10^{-4}$  -  $10^{-5}$  moles/liter, the straight proportion is usually upset in result of the extinguishing action created. By the excessive concentration.

In general, the quantitative analysis of luminescence consists of preparation of a set of standard specimen containing a known concentration of the substance investigated, and of measuring the intensity of their respective radiance. The obtained data will be used for plotting an analytical curve showing the luminescence intensity as function of the concentration. Having measured the radiance intensity of the analyzed sample. From the analytical curve we can establish the concentration of a substance in the sample.

In the quantitative analysis of luminescence, usually the natural radiance of the investigated substance is being utilized. When working with non-luminescing objects, luminescent reactions are being applied and by the radiance intensity of the resultant product, its concentration can be determined. Next, by using the conversion methods well known in the analytical chemistry, one can determine the concentration of the initial product of the said reaction.

For example, to determine the amount of oxygen in inert gases, the latter should be passed through a solution of colorless Leuco Base \* of the fluorescein pigment; the solution will oxidize, change into fluorescein which, in solution, has an intensive green luminescence. Having compared the intensity of the formed radiance with that of the solution luminescence, we can determine the concentration of fluorescein which formed in the process of the reaction. Simple calculations allow establishing the amount of oxygen passed through the solution, and that had oxidized the necessary amount of the Leuco Base.

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\* The leuco Bases are products of regeneration of some pigments which, as a rule, are colorless.

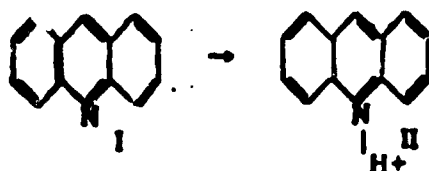
Quite often, an analysis cannot be successfully carried out due to the fact that the radiance intensity of the investigated substance can be determined not just from its concentration but also from a number of other factors. For example, the radiance intensity of a solution is being affected by: various processes of fading-out; absorption of a certain part of the exciting light by foreign admixtures; the secondary absorption of luminescence; etc. Therefore, when working out the technique for analysis of different groups of compounds, one should thoroughly investigate the nature of processes which might take place in solutions of these substances.

When carrying out an analysis, one should, first of all, follow all the rules concerning the excitation and the recording of radiance, as it has been described in #107. To receive reliable results, it is of great importance that both the standard and the investigated specimens were during the analysis subjected to rigidly similar conditions (excitation from the same source; an exactly the same position in the apparatus; both solutions in vessels of the same wall thickness, with a partly absorbed light of excitation; etc.). Moreover, it is vital that the spectral composition of radiance of either specimen was the same. For this purpose, the standard solutions of the very substance whose concentration we are about to investigate, serve as the standard. In those cases when it is impossible to prepare this kind of solution (instability of solutions, etc.) one can use standards of other substances instead, whose radiance by its spectral composition is similar to that of the investigated sample. Preliminarily, these standards should be graduated by the investigated substance solution whose concentration is known. Occasionally, the standards are consist of some types of luminescent glass (uranyl, and others) which are not subject to photo-chemical transformations, and emit a radiance constant in time.

The analysis results can be considerably distorted by existence of extinguishing ingredients in the sample. To eliminate their interference, diluted solutions ( $C \sim 10^{-5}$  moles/liter) should be prepared so that the concentration of those ingredients becomes negligible, and they will stop affecting the radiance itself. If the above method is not effective enough, one can compose standard samples using the same multi-component solvents which are contained in the specimen about to be analyzed. In case neither the composition of analyzed solution nor the concentration of the foreign admixtures are known, a certain amount of the investigated substance should be added to the investigated solution. By comparing the radiance intensity of the obtained mixture with that of the original solution, one can evaluate the extinguishing capability of the foreign ingredients.

In the analysis of substances with either basic or acid characteristics, the magnitude of "pH" greatly affects both the spectral composition and the radiance intensity. The magnitude of "pH" determines the condition of molecules in a solution; they can appear there either in a non-ionized state or as ions with opposite electric charges. Here, the radiance intensity of each of the molecule type can be extremely varied.

For example, molecules of a weak base of acridine in an alkaline medium ( $\text{pH} \sim 10$ ) remain in a non-ionized condition (I). When the value of "pH" goes down, they will gradually change into an ionized state, forming molecules of acridine (II). In the fifth normal HCL, the process will be completely terminated:



As a result, the spectral composition of the radiance will change; for an alkaline solution in the acid medium, from a violet-blue ( $\lambda_{\text{max}} = 425 \text{ m}$ ) it will turn into green ( $\lambda_{\text{max}} = 475 \text{ m}$ ). At the same time, the radiance intensity will drop to less than one-half. Therefore, it often becomes necessary to deal with the so called, "Buffer Solutions"; as an alternative, one can utilize the circumstance that starting with a certain value of "pH" of the solution, molecules of such compositions stop reacting to any change in the concentration of hydrogen ions. So, for example, the luminescence spectra of alcoholic solution of the 9 - aminoacridine will stop changing noticeably when the value of "pH" goes up to more than  $\text{pH} \sim 11$ . This kind of substances are being analyzed in solutions whose "pH" is beyond the above limit.

Above, we have indicated only the main factors which affect the accuracy of the quantitative analysis of luminescence. On the other hand, each of the investigated substances has its own specific properties which should be taken into account when working out the technique for its analysis.

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\* A buffer solution is a solution of salt, the salt and acid, or salt and alkali, in which the "pH" does not change its magnitude when either the concentration has been changed or acid or alkalis added in an amount below a certain limit.

A Quantitative Luminescence Analysis of the Termination of Chemical Reactions. This type of analysis concerns also the method of luminescent titration. This method consists of gradually adding small amounts of the substance-reagent from a buret into the investigated luminescent solution. The reagent is selected in such a way that after it had enter the reaction with the substance, it will form a compound which no luminescent properties. The reagent is being added for so long until the solution radiance will stop completely. Knowing the amount of reagent necessary for turning the investigated substance into a non-luminescent composition, by conversion we can determine its contents in the resultant solution. The above method presents a modification to the usual ones of chemical titration. The difference consists only in the following: in the luminescent titration, the process termination is being noted by the disappearance of its radiance, and not by a change in the solution color or by its having become cloudy. The main advantage of the luminescent method consists in its high sensitivity, a feature which makes it suitable for carrying out an analysis on highly diluted solutions.

In those cases when the process of radiance extinguishing by foreign mixtures has been thoroughly studied, this method can be also applied for a qualitative analysis. Here, the solution concentration can be evaluated by the degree of the radiance fading-out which will take place after a certain amount of a specially adapted extinguisher will be added to the analyzed solution.

The special features characteristic to the luminescence of a number of organic substances with their either acid or basic properties, allow a widespread use of luminescent indicators into the practice of chemical procedures. Their purpose similar to that of the ordinary indicators, is either indicating the end point of a chemical reaction or determining the concentration of hydrogen ions (the value of "pH") in the solution (table 38). The luminescent indicators differ from the ordinary ones in that at the end of a certain process, not their color will change but either their spectral composition or the intensity of their luminescence (Fig. 186).



TABLE 3B

Таблица 3Б

## ① Кислотно-основные индикаторы

Название индикатора ②	Структурная формула ③	Интервал pH перехода флуоресценции ④	Изменение цвета флуоресценции ⑤
⑥ 4-Оксакридон		1,3—3,2	зеленый—синий ⑦
⑧ α-Нафтиламин		3,4—4,8	отсутствует—синий ⑨
⑩ Акридин		4,8—6,6	зеленый—фиолетовый ⑪
⑫ β-Метилумбеллиферон		5,8—7,5	отсутствует—синий ⑫
⑭ Р-син		8,0—10,5	зеленый—синий ⑬
⑮ Чикаго-СС-кислота		10,0—12,0	фиолетовый—зеленый ⑭
⑯ 1,5-Нафтиллин-сульфо-кислота		12,0—13,0	синий—зеленый ⑮

- acid-basic indicators;
- Name of indicator;
- Structural formula;
- Interval "pH" of fluorescence conversion;
- Change of the fluorescence color;
- 4-oxacridone;
- Green-Blue;
- naphthylamine;
- None-Blue;
- Acridine;
- Green-violet;
- β-methyl umbelliferone;
- None-Blue;
- P-salt;
- Green-Blue;
- Chicago-CC-acid;
- Violet-Green;
- 1,5-naphthylamine-sulfo-acid;
- Blue-Green.

Thanks to the luminescent indicators we obtain a clear effect even if their concentration in a solution is very small. They are irreplaceable for the analysis of dark colored or turbid mediums (wine, oils, solutions of salts of some non-ferrous metals, etc.) where the ordinary indicators are hardly useful as their change of color cannot be noticed. At present, about 200 acid-basic luminescent indicators are known which cover the entire possible range within which the solution "pH" can vary. They are the derivatives of Benzene, naphthalene, coumarin, fluorescein, acridine, and other compounds. Most of the indicators display a blue-green radiance. Table 38 lists some of the more widely used acid-basic indicators.

Considerable less is known about indicators with a yellow-red luminescence. We could name here: the dimethylnaphthorhodine (pH = 3-3.6); the neutral red (pH = 5-7.4); 3,6 - dioxyphtalamide (pH = 6-8); and the acridine orange (pH = 8.4-9.2).

Working with luminescent indicators can become quite complex when the absorption spectrum of the analyzed specimen will superimpose itself on the luminescence spectrum of the indicator; then, the indicator radiance will become partly or fully absorbed. To prevent this, for each interval of the "pH" values, two indicators are being selected with luminescence of different colors. By using them one after another, we will obtain a correct result of the analysis.

In some rare cases, chemi-luminescent indicators are being used (Luminol, lucigenine, liphine, siloxen) whose performance is based on formation of a chemi-luminescent radiance when the "pH" value of a solution will change, and also when any kind of an oxidizer will appear in it. Their main superiority over the luminescent indicators consists in the fact that when working with them there is no need to subject the investigated solution to ultra-violet rays. To obtain reliable results, the analysis should be carried out at a certain constant temperature which highly affects the process of the chemi-luminescent reaction.

#### #110. Polarization Methods of the Luminescence Analysis.

Besides a qualitative and quantitative analysis of the substance composition, the luminescent methods aid in solving many other important problems associated with the structure analysis of complex molecules and crystals. Particularly promising in this respect are the polarization methods. By applying them, one can: determine a mutual disposition of the absorbing and emitting oscillators in molecules as well as the orientation of emitting oscillators in relation to the molecular axes; establish the relation between the symmetry of molecules and the polarization; determine the multi-polarity of elementary emitters of the molecules; and also measure the volume of investigated molecules and the duration of their radiance.

Determining the Mutual Disposition of Absorbing and Emitting Oscillators. The behaviour of real molecules can be approximated by analyzing the performance of various types of elementary emitters. Mostly, the molecules can be linked to linear oscillators (dipoles). V. L. Levsnin and F. Perren have established that the degree of luminescence polarization is a function of angle " " between the oscillator of emission and that of absorption, and can be presented in the following formula:

$$P = \frac{3\cos^2\alpha - 1}{\cos^2\alpha + 2} \quad (20.4)$$

It turned out that the degree of polarization depends on the wave-length of the exciting light. This interdependence was thoroughly studied by Vavilov who called it a polarization spectrum. He demonstrated that, when  $\lambda_{\text{exc}}$  goes down. The degree of polarization will drop drastically, frequently even changing its sign; later, it will go up again and sometimes reaches a second maximum. P. P. Feofilov has established that that is a certain relation between the polarization spectra and those of absorption (Fig. 205).

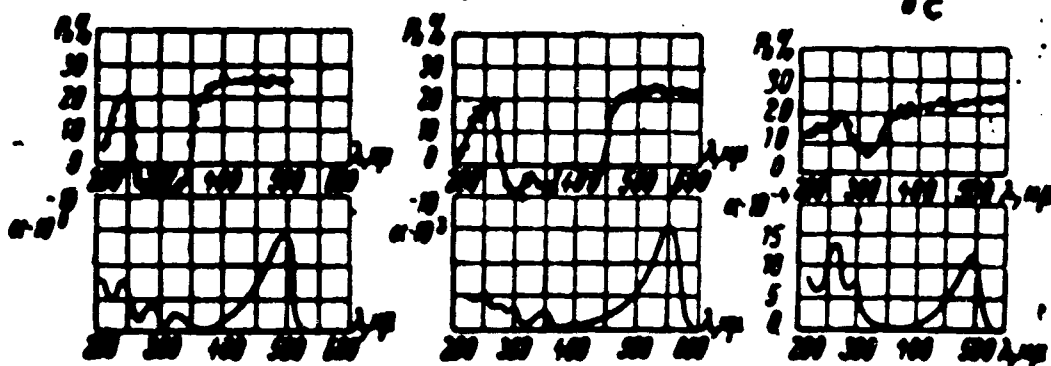


Fig. 205. Polarization spectra (top curves) and spectra of absorption (bottom curves) of pigment solutions: a-fluorescein; b- Rhodamine B extra; c- acridine orange.

Within a single band of absorption the degree of polarization does not change much. This means that each electronic transition is matched by its own absorption oscillator. Considering that the individual bands of absorption superimpose each

other, transition from one value of polarization to another proceed continuously. Having measured the degree of the luminescence polarity when excited in different zones of absorption, by formula (20.4) one can establish the relating disposition of the oscillators of absorption and those emission in the investigated molecules. Polarization spectra were used for the research on the structure of numerous organic compounds (naphthalene, anthracene and its derivatives, polyenes, porphyrins, chlorophyll, etc.)

Another important problem which so far has been solved but few compounds, is establishing the orientation of absorption oscillators in relation to the molecular axes.

In the case of molecular mono-crystals, the polarization of luminescence can be determined by both orientation of the emission oscillator in relation to the molecule axes, and by orientation of the molecule itself in the crystal lattice. If one of these factors is known, then the other can be determined by the polarization of radiance. Thus, by the orientation of molecules in the lattice of mono-crystals of naphthalene, anthracene, stilbene, and other compounds. By having measured the luminescence polarization of the above crystals, we could determine the orientation of their emitting oscillator in relation to the molecular axes. On the other hand, having compared the polarization and absorption spectra of the solutions, we can establish the orientation of the oscillators of absorption and emission, respectively, in relation to the molecule axes. Next, having measured the polarization diagrams (see below), we can determine the orientation of molecules in the crystal lattice. For example, using the above method, N. D. Znevandrov has determined the orientation of anthracene molecules in the lattice of its mono-crystals.

#### How the Symmetry of Molecules Affect the Magnitude of the Terminal Polarization of Luminescence.

In those cases when the solution is highly viscous, and all the outside depolarizing factors have been eliminated, the luminescence polarization  $P_0$  is at its maximum, and is called the "Terminal Polarization". It turned out that value of the terminal polarization is determined by the symmetry of molecules; the more symmetrical the molecule the lower is the value of the corresponding  $P_0$ . For instance, for flat molecules with an axis of symmetry of the "n"- order, at 90° to their surface:

$$P_0 = \begin{cases} \frac{1}{2} & \text{when } n \leq 2 \\ \frac{1}{n} & \text{when } n > 2 \end{cases} \quad (20.5)$$

Thus, if a flat molecule has a symmetry axis of the third order, its  $P_0 \leq 0.14$ . For non-symmetrical molecules and those with a symmetry axis of the second order,  $P_0 \leq 0.5$ . For example,

molecules of benzene have a symmetry axis of the sixth order, and their  $P_0 \approx 0.08$ ; molecules of the 3,6-diaminoacridine have a symmetry axis of the second order, and for their solution the  $P_0 = 0.40$ .

**Polarization Diagrams.** The elementary emitters of absorption and emission, not always can be compared to linear dipoles. In some cases, they have characteristics of an electric quadrupole or a magnetic dipole. Vavilov suggested that the multipolarity of elementary emitters should be determined by the polarization diagrams which represent the polarization of luminescence as a function of both the direction of observation and position of the exciting light electric vector.

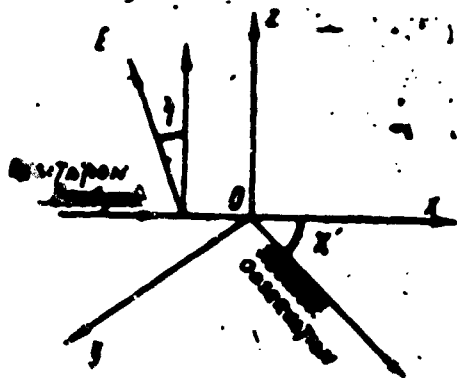


Fig. 206. Observing the polarization diagrams of photoluminescence.

Fig. 206 shows the method of observing polarization diagrams. Angle  $\alpha$  characterizes the oscillation gradient of the electric vector in relation to the vertical axis; angle  $\beta$  characterizes the direction of observation in relation to propagation direction of the exciting light rays. Having measured the degree of polarization for different values of angles  $\alpha$  and  $\beta$ , we will plot the polarization diagrams. Fig. 207 shows the polarization diagrams:

$$P = f(\alpha) (\beta = 0 \text{ and } \frac{\pi}{2}) \text{ and } P = f(\beta) (\alpha = 0 \text{ and } \frac{\pi}{2}),$$

calculated by Vavilov for various combinations of elementary emitters similar to electric dipoles and quadrupoles. As we can see, the diagrams are very specific, and can be used for establishing the nature of elementary emitters of the absorption and emission.

The method of polarization diagrams can be applied for solving the problem of multipolarity of elementary emitters not just in molecules but also in crystals. For example, when exciting radiance of cubical fluorite ( $\text{CaF}_2$ ) crystals in zone of the first absorption band, the processes of both absorption and emission can be defined by electric linear dipoles. In other cases, the nature of elementary emitters can be more complex.

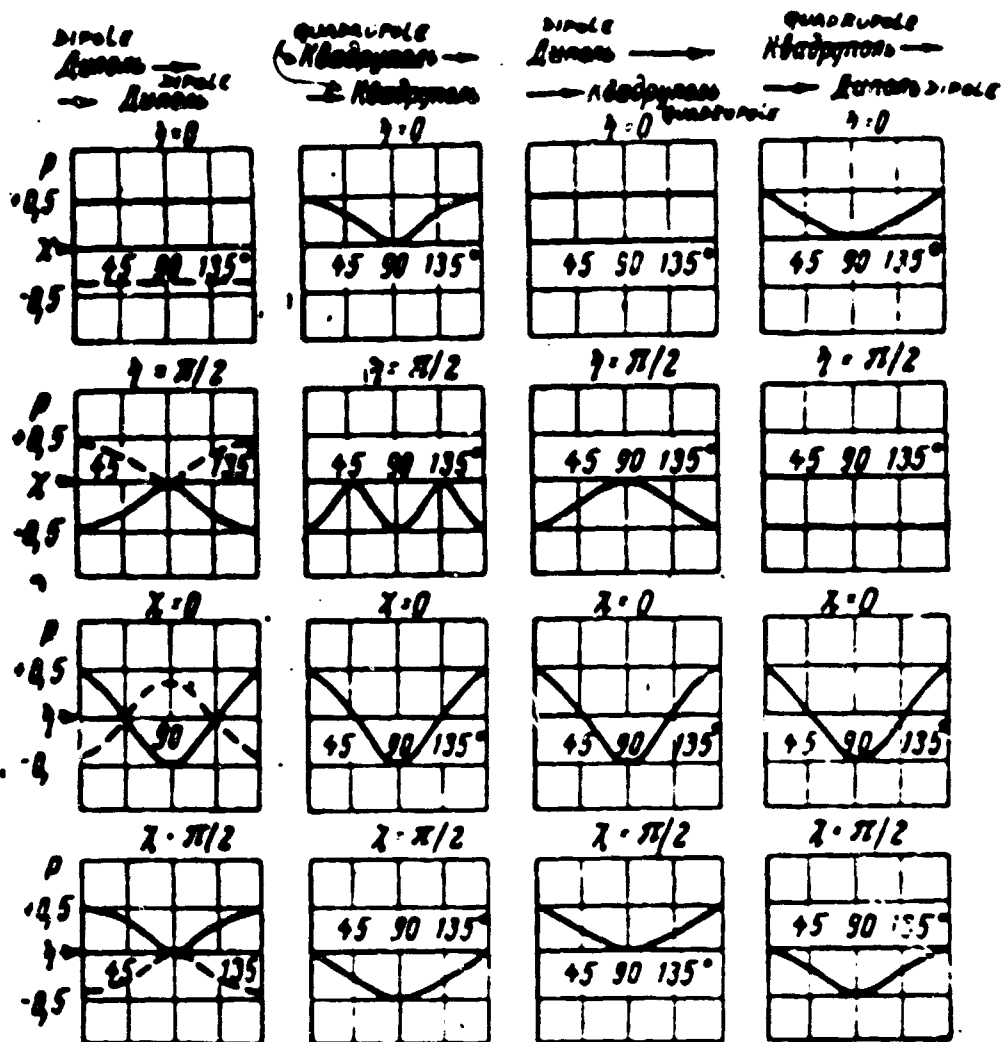


Fig. 207. Polarization Diagrams of various, and variously oriented elementary electric emitters. Solid curves- when the respective axes of absorbing and emitting oscillators are parallel; dotted curves- when the axes are at right angle to each other.

Determination of Molecular Volumes and " $\epsilon$ ". Having the polarization readings we can determine the volume of investigated molecules. The calculation is based on a formula worked out by Levshin and Perenne:

$$\frac{1}{P} = \frac{1}{P_0} + \left( \frac{1}{P_0} - \frac{1}{3} \right) \frac{TA_1}{V_1} \quad (20.7)$$

Where:

- P- Degree of polarization in the conditions in which the experiment is being carried out;
- P<sub>0</sub>- Terminal Polarization;
- T- Temperature;
- $\eta$ - Viscosity of solution;
- R- Gas constant;
- V- Volume of a Gram-molecule;
- $\tau$ - Average duration of the excited state of molecules.

After we have plotted  $1/p$  on the ordinate axis, and  $T/\eta$  - on the abscissa, we will obtain a straight line (Fig. 208). The segment chopped off by the curve from the ordinate axis determines the magnitude of  $1/P_0$ , and the tangent of angle of its slant in relation to the abscissa axis, with equal:

$$\lg \tau = \left( \frac{1}{P_0} - \frac{1}{P} \right) \frac{RT}{V} \quad (20.7)$$

When " $\tau$ " has been measured regardlessly, we can estimate the molecule volume "V" from the above formula. In this way, one had determined both of the molecular volume and solvate shells of many phthalamides, anthracenes and acridines.

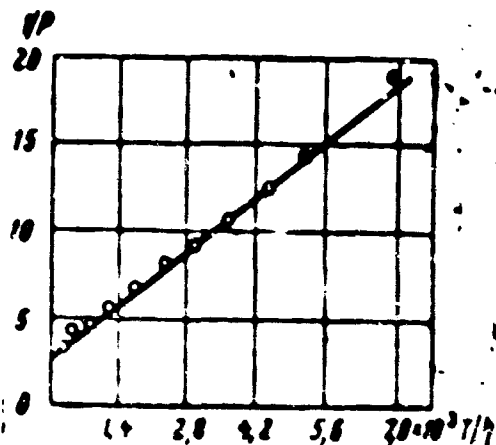


Fig. 208. Depolarization of luminescence of fluorescein in glycerine when heated.

On the other hand, having independently measured the "P" and "V" (the value for "V" can be obtained from experiments on diffusion), we can determine the value for " $\tau$ ". In this way, A. N. Sevchenko has obtained the values of " $\tau$ " for solutions of a number of pigments. By applying the above method for metering of " $\tau$ ", one can get away without using the hard-to-get fluorometers; usually, the obtained results are pretty accurate.

### §11. Luminescence Analysis of Non-organic compounds.

The number of pure, non-organic compounds capable to luminesce, is very limited. Some of them will luminesce only when in crystalline form,

others will produce radiance only in solutions. These compounds include: salts of the rare-earth elements (R.E.E.); uranyl salts (including the uranyl group  $UO_2$ ); some complex salts of heavy metals (TL, Sn, Pb); platinicyanic salts [with the group  $Pt(CN)_4$ ]; tungstates and molybdates ( $XWO_4$  and  $XMoO_4$ , where the

alkali-earth metals serve as cations X); aluminates ( $\text{Al}_2\text{O}_3$ ); chromates ( $\text{Cr}_2\text{O}_3$ ); and a number of precious stones.

By far the biggest part of all luminescent non-organic compounds form the crystalphosphori whose necessary element comes in form of admixtures-activators; the latter are deforming the crystalline lattice of the basic substance, and form the centers of radiance. Occasionally, the radiance exciting defects of the lattice form in the very process of preparing the phosphori, with no special ingredients added. Due to complexity of the radiance process of crystalphosphori, and its dependence on many hard-to-be-accounted factors, a chemical luminescence analysis of the above compounds is being used but rarely. Mostly, it is used when working with minerals which are crystalphosphori of a natural origin.

From a practical point of view, of all the pure, luminescent, non-organic substances, the rare-earth and the uranyl compounds are the most important. Their solutions display a characteristic radiance which has been thoroughly investigated; for these compounds, both the qualitative and quantitative analysis of luminescence have been worked out.

#### Luminescence Analysis of the Rare-earth Compounds.

Special Features of the Rare-earth Elements. The R.E.E. (with their atomic number from 57 up to 71) occupy a special place in the Mendeleev's periodic system. When the atomic number becomes higher, the inner electronic shell "4f" (from zero for lanthanum up to 14 for Ytterbium) becomes filled up. On the other hand, the outer shell of all R.E.E. retains the same structure; this is why all of them are chemically similar. However, the optical characteristics of the R.E.E. differ from each other considerably. This can be explained by the fact that the spectra of both absorption and luminescence are associated with transitions between the terms "4f" of the shell.

By the nature of their luminescence spectra, the R.E.E. can be divided in two groups. The first group, the so called "Gadolinium Group", includes: Samarium (Sm); Europium (Eu); Gadolinium (Gd); Terbium (Tb); and Dysprosium (Dy), all of which are occupying a central place among the R.E.E. Their solutions produce very characteristic, narrow bands of luminescence which at low temperatures will split into separate lines. The second group, the so called "Cerium Group" includes: Cerium (Ce); Praseodymium (Pr); Neodymium (Nd); Ytterbium (Yb) which all are occupying the extreme place among the R.E.E. Their solutions produce wide, diffused bands of luminescence.

At the same time, some of the R.E.E. do not produce any luminescence at all (Holmium Ho and Lutecium Lu), the radiance of others can be seen only in special conditions. For example radiance of Ytterbium will form only at a temperature of the liquid air; the luminescence of Thulium (Tu) can be excited only if it is either immersed into a solid solution of ( $\text{ZnS} \cdot \text{Tu-phosphori}$ ).



Special Features Characterizing the Spectra of Luminescence and Absorption of the R.E.E. The particular uniqueness of the R.E.E. Luminescence spectra comes very handy for the analytical is greatly purposes. However, the luminescence analysis is greatly hampered by the circumstance that the luminescence spectra of R.E.E. (the ratio of intensities of individual lines) highly depend on concentration of the investigated element, on the presence of other R.E.E., and on the temperature. Position of the bands will also change, depending on nature of the main substance in which the analyzed compound is located: on the distance between the anions and cations in a crystal, and on the crystal constant of the main substance lattice. Moreover, the luminescence spectra of the R.E.E. are very sensitive to the influence of various foreign admixtures. For instance, the existence of even traces of nitric acid in the solution is sufficient in order to fully extinguish the luminescence of Tb ions. On the other hand, Eu will luminesce in a diluted solution only in presence of traces of  $\text{SO}_4^{2-}$  ions.

In the Gadolinium group, the most intensive radiance in diluted solutions is produced by Tb and Gd itself. The latter displays only a single, narrow, ultra-violet strip of luminescence in the zone of 311 m $\mu$ . The luminescence spectrum of Tb is more copious: it consists of seven narrow strips positioned predominantly in the long-wave part of the visible spectrum. Their half-width is 2-5 m $\mu$ . The radiance of Eu, Sm, and Dy solutions has a low intensity, consequently, the sensitivity of their analysis on the luminescence spectrum is rather low. For example, in a solution the Tb will be detected if its concentration is  $\sim 10^{-8}$  gram/milliliter for Eu the extreme concentration is only  $\sim 10^{-4}$  gram/milliliter. Nevertheless, both Eu and Sm are excellent activators for crystalphosphors; in a concentration of only  $10^{-7}$  gram/gram, they will produce a bright and extremely characteristic radiance.

In the second group, the most intensive radiance is produced by "Ce". Its spectrum appears as a wide band which embraces the entire near ultra-violet zone from 313 up to 400 m $\mu$ . A high radiance intensity of the diluted solutions of  $\text{Ce}^{+++}$  permits a reliable detection of this element presence when its concentration is as low as  $10^{-8}$  gram/milliliter.

All the R.E.E.-s are characterized by a solid band of absorption in the far ultra-violet part of the spectrum. Therefore, they are usually being excited by either an electric arc or an electric spark which both have an intensive emission in this spectral zone. Sometimes, the R.E.E.-s are being excited by means of cathode rays. For instance, the Indian scientists have applied the above method for detecting traces of R.E.E. in fluorites, calcites, limestones and in the ashes of coal mined in India,

All the above said serves as a proof that the luminescence analysis of R.E.E.-s presents a hard problem due to their complete lack of radiance, some elements are not suitable for analysis at all, others require an elaborate technique. Right now, basically used are the methods of a qualitative and, sometimes, a semi-quantitative luminescence analysis of the R.E.E.-s.

The method of Pearls. One of the recommended methods for a qualitative analysis of R.E.E.-s is the method of pearls. Here, the R.E.E.-s are placed in the pearls of either borax or phosphoric acid. In these media, the salts of many R.E.E.-s (Sm, Dy, etc.) produce a very intensive radiance whose spectrum consists of a number of characteristic bands. The Ce salts have a solid spectrum whose maximum is close to 450 m $\mu$ . To detect the small amount of Eu, one has to produce pearls by fusing the basic substance (sodium chloride or strontium chloride) with the investigated specimen: pearls obtained on the base of sodium chloride produce a bright, violet-blue radiance, those on the strontium chloride - a violet radiance. After having prepared a set of standard pearls containing a known concentration of Eu, one can determine its approximate quantitative composition in the analyzed pearl. There are also other methods which permit to fast determine the approximate contents of Eu in R.E.E. oxides. Sensitivity of this method reaches  $\sim 0.005\%$ , its accuracy  $\pm 10 - 20\%$ .

In some cases, sensitivity of the pearl method turns out to be not high enough; it can detect Ce with a concentration down to  $\sim 10^{-4}$  gram/gram, and Sm with a concentration down to  $\sim 10^{-3}$  gram/gram. Moreover, due to lack of radiance, the pearl analysis of La, Pr, Nd, Er is unattainable.

Introducing the R.E.E.-s into Tungstate and Molybdates.

More sensitive than the above is the method where R.E.E.-s are fused with either calcium tungstate ( $\text{CaWO}_4$ ) or calcium molybdate ( $\text{CaMoO}_4$ ). In such a solid solution, the R.E.E.-s also have a characteristic, either ruled or striped spectrum which only little is affected by the substance concentration, foreign admixtures or the presence of other R.E.E.-s. The  $\text{CaWO}_4$  itself produces a sharp, blue luminescence which forms a background hampering the observation of the rare-earths radiance; this interference can be reduced by heating the specimen up to 1000 Centigrade, when the temperature-induced extinguishing of rare-earths is not yet noticeably affected.

In the above method, the excitation is being effected by a mercury, low-pressure discharging tube. The investigated substance should be deposited on the inner surface of the tube which then is placed in a cylindrical oven where radiance of the  $\text{CaWO}_4$  will be suppressed. The luminescence will be watched through a window in the oven. By studying the radiance in the ultra-violet, visible and nearer infra-red parts of the spectrum, we can carry out analysis on many R.E.E.-s and their

combinations. For example, the described method allows detecting  $\sim 10^{-7}$  gram of Sm in 1 gram of  $\text{CaWO}_4$ . However, some R.E.E.-s could not be detected by this method.

The Method of Additives. For phosphori on a base of  $\text{CaS}$ ,  $\text{SrS}$ , and also on the base of  $\text{ZnS}$ , the R.E.E.-s can serve as activators, and can determine the nature of radiance. In this way, we can detect minute amounts of R.E.E.-s in the sample. For instance, to solve a number of practical problems, it is important to obtain Thorium, and its compounds, with extremely small contents of R.E.E. admixtures (not more than  $10^{-5} - 10^{-4}\%$ ). Such minute contents of R.E.E. can be detected only by means of a luminescence analysis using the method of additives. Principle of the above method is as follows. A set of crystallophosphori should be prepared, with the Thorium to be analyzed as their base; the Thorium is turned into Thorium sulfate or Thorium oxide. The R.E.E. activators (Gd, Sm, Eu) are being introduced in a form of additives of a different concentration. It has been established that, in a wide range of concentration, there exists a certain ratio between the brightness of the crystallophosphori radiance and the concentration of the R.E.E. contained therein either as a natural ingredient or an additive. Then:

$$\frac{I_1}{I_2} = \frac{C_x}{C_x + C_a} \quad (20.8)$$

Where:  $I_1$  and  $I_2$  - the respective brightness of the phosphorus, without or with an additive which has a concentration  $C_a$ ;

$C_x$  - The R.E.E. concentration to be found.  
In general, for any value of  $C_a$ :

$$I = A(C_x + C_a) \quad (20.9)$$

Where:  $A$  - the radiance intensity of the phosphorus when the concentration of the R.E.E. equals 1.

Having plotted the values for "I" on the axis of ordinates, and those for " $C_a$ " on the axis of abscissae, for a series of phosphori we will obtain a straight line whose inclination permits estimating the value for "A", and the sector on the abscissae axis between the point where it is bisected by the straight line, and the center of coordinates, determines the value of  $C_x$  (Fig. 209).

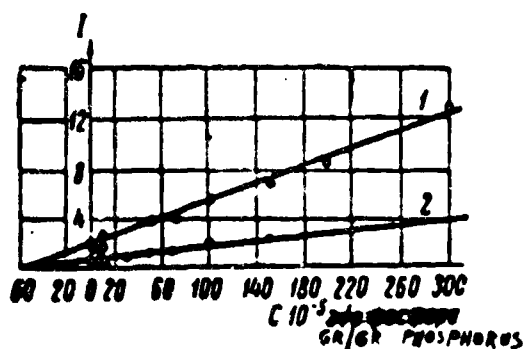


Fig. 209. Quantitative determination of samarium in Thorium; metallic thorium: 1- pure, 2- artificially contaminated with a R.E.E.

It is important that the additives  $C_a$  are commensurated with  $C_x$  (they should differ from the latter several times over). Therefore, at first, by the relative radiance intensity of three phosphori each with a drastically different concentration of the investigated R.E.E., the order of magnitude of the  $C_x$  in a non-activated phosphori should be estimated. Next, a set of phosphori should be prepared, with various values of  $C_a$ , and by the intensity of their radiance the  $C_x$  can be determined. Radiance of the phosphori is being excited with an electric spark, using a phosphoroscopic apparatus. It has been established that in the thorium-phosphori activated by Gd, Sm, and Eu, the foreign contaminants Sm, Eu, Dy, Fe, Mo, Cu, and also their combinations, which exist there in a quantity of  $10^{-5}$   $10^{-3}$  gram/gram, practically do not affect the analysis accuracy, but noticeably lower its sensitivity (Fig. 209). The method of additives is being applied also for a quantitative determination of Gd in metallic Be.

There are also known other, more specific methods for determination of some R.E.E.-s. For example, there is a quite sensitive method of determining a R.E.E. in calcium oxide which should be placed in the colorless flame of hydrogen. Even with an insignificant concentration of the R.E.E., the slow electrons in the flame will excite a noticeable radiance.

#### Luminescence Analysis of the Uranyl Compounds.

Among the uranyl compounds, the uranyl salts embracing the uranyl group  $UO_2$  have a significant capability of luminescing. Their luminescence spectra are very characteristic, and consist of a number of bands at an approximately equal distance from one another. Usually, the molecules of uranyl compounds contain a great amount of water of crystallization which to a great extent affects their spectra of luminescence.

Characteristics of spectra also greatly depend on the contents of the investigated salt and the structure of its crystal. Radiance of the uranyl salt solutions is considerably weaker, and their spectra more washed out.

Glass tinted with uranyl salts luminesce brightly. The radiance intensity of uranyl compounds goes up significantly when they are cooled down to the temperature of the liquid nitrogen. Fig. 210 shows the luminescence spectra of uranyl sulfate  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  in both a crystal form and solution of sulfuric acid at a room temperature.

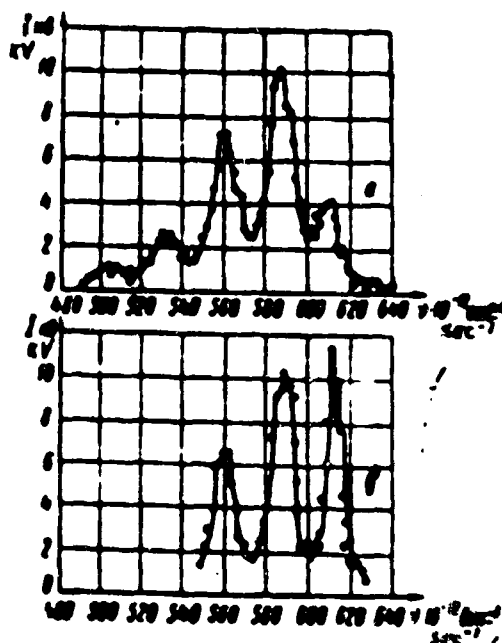


Fig. 210. Luminescence spectra of uranyl sulfate:

- A- crystalline  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ;
- B- solution  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  in sulfuric acid.

A qualitative luminescence analysis of uranyl compounds is easy to perform as they produce an intensive and characteristic radiance. By having accurately measured the wave-lengths of bands of the luminescence spectrum, one can establish the nature of the investigated salt.

In a quantitative luminescence analysis, small concentration of the uranyl compounds are usually determined by the method of pearls. The luminescence intensity of the uranyl compounds includes when fused, into the pearls of either borax, NaF or KF in a wide range of concentration (up to  $1 \cdot 10^{-6}$  gram/gram NaF) will vary with their respective concentration. A quantitative determination of uranyl contents

in comparing the radiance intensity of the pearls to be analyzed with the of the standard pearls in which the concentration of uranium is known.

When excited by a mercury line  $\lambda = 365 \text{ m}\mu$ , the pearls on a NaF base produce a yellow-green luminescence ( $\lambda_{\text{max}} = 555 \text{ m}\mu$ ). Radiance of a similar spectral contents can form also with Niobium; however, it will be excited by a more short-wave radiation, as for instance, by a resonance mercury line with  $\lambda = 253.7 \text{ m}\mu$ . In pearls based on KF, no radiance of Niobium can be excited. However, the luminescence intensity of uranyl compounds in these pearls is considerably lower than in those with NaF.

In some cases the pearls are being made of a more complex mixture, consisting of NaF,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , all taken in a certain proportion. Here, we can lower the temperature at which the pearls are being produced, from  $1,100^\circ$  down to  $600^\circ$  Centigrade.

For a higher accuracy of the analysis, it is important that the technique of pearl preparation is standardized: the pearls should be made of equal size; their fusing should proceed for a certain predetermined time; one should take into account the drop of intensity of the pearl radiance. A process which can be observed within the first 12 hours after they have been prepared.

The radiance intensity of uranium compounds in pearls can be greatly affected by presence of foreign admixtures many of which turn out to be luminescence extinguishers. For instance, Cr, Mn, Co, Ni, La, Pt, Au, Ce, Pr, Nd are all strong extinguishers; less active in this respect are: Fe, Cu, Zn, Sn and Th; Tl and W are mild extinguishers. Other elements practically do not affect the luminescence intensity of pearls at all. For example, the presence of neptunium and plutonium does not hamper an analysis on uranium.

A number of other foreign admixtures have an extinguishing capability, too. Particularly, all the tinted oxides (Fe, Co, Ni, Mn, Cr, etc.) turn out to be quite strong extinguishers. When carrying out a quantitative analysis, the strongest extinguishers should be eliminated from the investigated specimen chemically.

The pearl method is being widely used in the luminescence analysis on ores containing less than 0.01% of uranium. When metering photoelectrically, the above method permits detecting the amounts of uranium from  $10^{-5}$  down to  $10^{-10}$  gram in 0.3 gram of NaF. Here, the analysis accuracy reaches  $\sim \pm 5\%$ . When metering visually, the accuracy drops down to  $\pm 30\%$ .

#### Luminescence Analysis of other Non-organic Compounds.

When carrying out the luminescence analysis on many non-organic compounds, they often utilize the luminescent reactions. For example, to determine the amount of indium, they perform a reaction between anions of IN Brg and cations of rhodamine pigment 3 B. The obtained compound is then extracted by means of Benzene. By reading the radiance intensity of the above solution, one can establish its contents of In down to  $2 \cdot 10^{-8}$  gram in 5 milli-liter of solution. Recommended are also other reagents which form luminescing complexes with various cations: 8-hydroxyquinoline for Li and Al; morin for Be, Al, Sn, Zr; rhodamine B for Ag, Ga, Tl, Te; 3-oxiflaval for Zr, Hf; trioxylfluorone for Th; Benzoin for B; etc.

As indicated before, many metals can serve as activators in crystallophosphors which produce a strong luminescence. This circumstance can be used during the analysis. For example, when analyzing antimony, a drop of the investigated sample should be deposited on the non-luminescent calcium oxide, during the calcination in presence of Sb, a crystallophosphor  $\text{CaO} \cdot \text{Sb}$  forms whose color of luminescence depends on the concentration of antimony. The above method permits a qualitative detection of down to  $1 \cdot 10^{-12}$  gram of Sb ions in a drop of

solution ( 0.01 milli-liter).

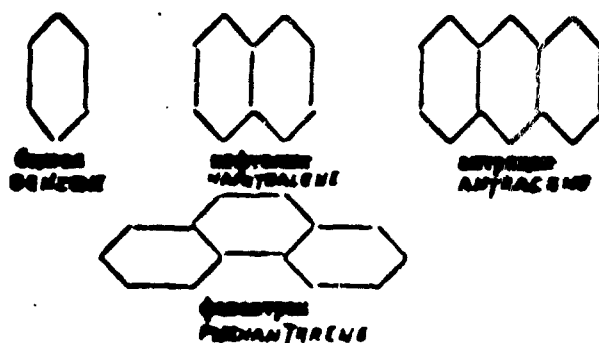
By creating the crystalphosphorus KI Sn, we can detect  $\text{Sn}^{++}$  in a solution. For this purpose, a drop of the solution and a drop of KI shall be deposited either on a filter paper or on a non-glazed porcelain plate. If Sn is present, the spot will produce a bright-yellow luminescence. The above method allows detecting when on paper- 0.02  $\mu$ -gram of Sn if diluted in ratio 1: 5.10<sup>5</sup>; and when on porcelain- 0.0002  $\mu$ -gram of Sn if diluted in ratio 1:1.5.10<sup>6</sup>. By using the method of forming the crystalphosphori, one can detect microspic amounts of Hg, Tl, Bi, Pb and other elements.

Known is also a luminescent method of establishing the contents of chromium in synthetic rubies whose characteristics are being determined by its concentration. Ions of chromium ( $\text{Cr}^{+++}$ ) affect the red tint and the intensive luminescence of rubies. When their concentration goes up, the luminescence spectrum will change drastically; the percentage of the long-wave infra-red emission will increase. At the same time, the ratio of intensity of the spectrum infra-red part to that of the chromium doublet ( $\lambda = 692.7$  and  $694.2 \text{ m}\mu$ ) will go up by the exponential law. Having measured this ratio, we can determine the contents of chromium in any sample with an accuracy of  $\sim \pm 5\%$ , without any special processing of their surface required.

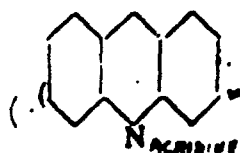
Such an analysis is very important in the manufacture of precision apparatus and, particularly, for the watchmaking industry.

#### §112. Luminescence Analysis of Organic Compounds.

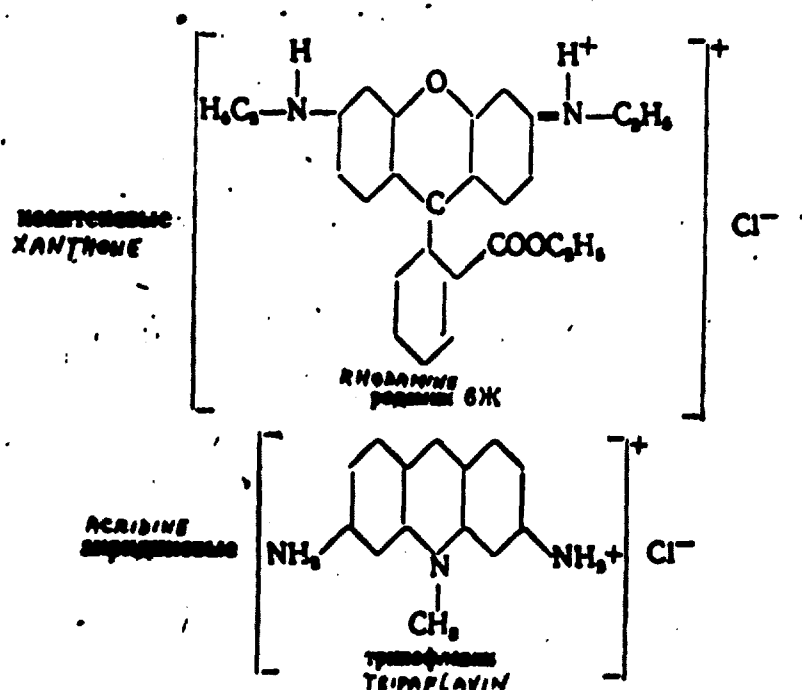
Numerous organic substances have a capability to luminesce. They include the most simple aromatic compounds:



Many of their derivatives, some heterocyclic compounds



(Acridine and its derivatives), the chain-like compounds with conjugate bonds  $(R-(CH=CH)_n-R_1)$ , where R and  $R_1$  - groups of  $CH_3$ ,  $C_2H_5$ ,  $C_6H_5$ ,  $C_6H_4$ , etc.), some pigments:



and many other compounds.

Some organic substances can luminesce when in vapor, liquid or solid state, others - only when in solutions.

The luminescence spectra of solutions of the organic compounds appear as wide bands, at either the visible or the nearer ultra-violet zone (Fig. 187). In spectra of some substances one can see their oscillating structure which is particularly distinct at low temperatures. Different factors are greatly affecting the luminescence properties of solutions of the organic compounds. For instance, both the shape and distribution of the luminescence bands may depend on the value of the solution "pH" (Fig. 186), on nature of the solvent, and the temperature. Moreover, the luminescence output may depend on the existence of foreign extinguishing admixtures in the solution, and the latter's concentration. All these factors should be taken into account when working out the analysis technique.

The luminescence methods are being used for both the qualitative determination of various organic substances, particularly

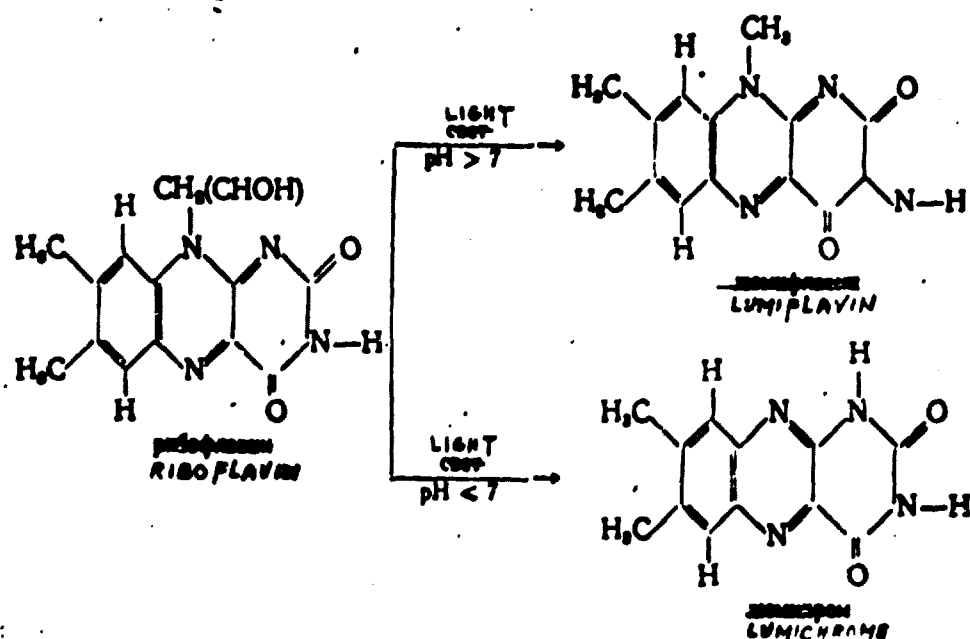


of the compounds affecting the organisms of the human and animal world. Included here are: vitamins, hormones, pigments, antibiotics, cancerogenic substances, and many others. Also, the methods of the luminescence analysis play an important role in the research on oils and bitumens.

#### The Luminescence Analysis of Biologically Active Substances

Luminescence Analysis of Vitamins. The vitamin B<sub>2</sub> (C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>) called "riboflavin" or "Lactoflavin" is intensively luminescing in a solution. It is contained in liver, milk, eggs, vegetables, and plays an important role in the metabolism of the human body. Its luminescence spectra appears as a washed-out band with its maximum at  $\lambda = 535 \text{ m}\mu$ .

Riboflavin can be detected by their photochemical reactions created by the exciting light. When excited, the riboflavin which usually remains in either a neutral or acidulous solution turns into lumichrome producing a blue luminescence. In an alkaline solution, under an ultra-violet radiation, riboflavin will turn into lumiflavin which produces a sky-blue radiance:



It is difficult to carry out an analysis on vitamin B<sub>2</sub> because one has to determine its significant amount in such complex systems as the foodstuff, plant tissue, etc. For each case an individual method has to be worked out.

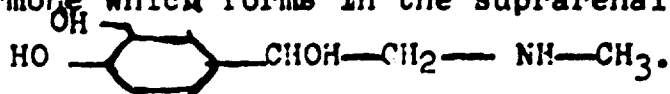
A quantitative analysis of the B<sub>2</sub> vitamin is carried out in a complex way. From the investigated sample it has to be transformed into a water solution; then it should be absorbed on special adsorbents (lead sulfide, frankonite, etc.), from

which it is transferred into the pyridine solution. By comparing the radiance intensity of the pyridine solution with that of the standard one, one can determine the concentration of the B<sub>2</sub> vitamin in the sample. However, such a analysis is very time-consuming. Therefore, simplified methods are often used which allow a quantitative estimate of the B<sub>2</sub> vitamin contents. For instance, when establishing the vitaminosity of milk, the riboflavin should be transferred into acetone solution whose radiance intensity will be compared with that of a standard cube made of uranyl glass. The cube radiance should be preliminarily graduated by the standard solutions containing a know concentration of riboflavin.

The human body is greatly affected by vitamin B<sub>1</sub> (C<sub>12</sub>H<sub>19</sub>ON<sub>4</sub>SCl<sub>2</sub>) called either thiamin or aneurin, which does not produce luminescence. However, it can be detected by a thiochrome method which consists of oxidizing the B<sub>1</sub> vitamin by potassium ferricyanide K<sub>3</sub>[Fe (CN)<sub>6</sub>] after the former has been turned into a aqueo-alkaline solution. In result of the above reaction, a new substance will be created- the thiochrome which produces a very intensive, blue luminescence ( $\lambda_{\max} = 460-470 \text{ m}\mu$ ). From the obtained mixture, the thiochrome can be separated by using the isobutyl alcohol. By comparing the radiance intensity of the thiochrome solution with that of the standard, one can determine its concentration. Then, by a calculation one can determine the B<sub>1</sub> vitamin concentration in the investigated sample.

Majority of the other vitamins, as, for example, vitamin C (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>- ascorbic acid), vitamin E (C<sub>29</sub>H<sub>50</sub>O<sub>2</sub>- toferol), have their own radiance. Some of the non-luminescing vitamin (vitamin A-C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>) can be turned into luminescing compounds by means of a chemical reaction. Thus, the luminescent methods can be used also for analysis of these compounds.

Luminescence Analysis of Hormones. Luminescence methods can be also used for analysis of various hormones\*. For instance, widely applied is the luminescence analysis of adrenaline - an important hormone which forms in the suprarenal glands



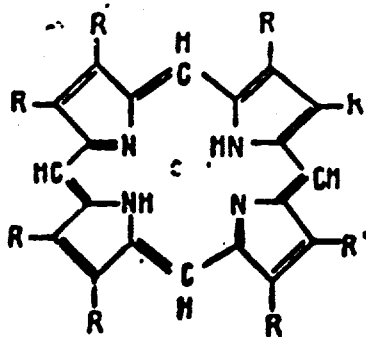
The above compound is being applied for boosting the blood pressure, for heart diseases, etc. An intensive, yellow radiance can be seen only in an alkaline solution of the adrenaline. However, the radiance is emitted not by the adrenaline itself but by the product of its oxidation. Th analysis becomes complex due to the circumstance that the oxidation process does not stop here but goes on and develops continuously until the solution will completely lose its luminescent capability. The second part of the process can be effectively retarded if the analysis is being carried out in a solution of the concentrated alkali (1951).

\* Hormones - Biologically active substances discharged into the blood and the tissue liquid by the inner secretion. They greatly affect the metabolism in both human and animal bodies.

Then, by the radiance intensity of the solution, we determine the quantitative contents of the primary products of the adrenaline oxidation, and, by a comparison, the adrenaline concentration.

The luminescence methods are being used also for analysis of sex hormones - the estrogenic substances many of which (for instance, the folliculines) produce a sufficiently intensive radiance in the short-wave part of the visible spectrum.

Luminescence Analysis of Pigments. Many pigments are producing a characteristic and intensive radiance,\* too. The most important of them are the porphyrins (derivatives of chlorophyllin)



Where R - the methyl group of  $\text{CH}_3$  or some other radicals. They are discharged from blood, liver, brain and other biological substances contained in bodies of animals and birds. The porphyrine radiance is located in the long-wave part of the visible spectrum (between 600 and 800 m $\mu$ ), and consists of two, three or four characteristic narrow strips. Different porphyrines have their individual radiance strips very close to one another, and thus not easily identifiable.

The porphyrines are bases. Therefore, their luminescence spectra are highly dependent on value of "pH" of the solution: lower pH will shift them towards the short waves. In different porphyrines, the radiance intensity depends on the pH value in a different way. This feature can be utilized for the purpose of their separation and identification. As an example, Fig. 211 shows the corresponding curve for three different porphyrines.

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\* Pigments - the tinted organic substances contained in the tissues of living organisms, and important for their functioning.

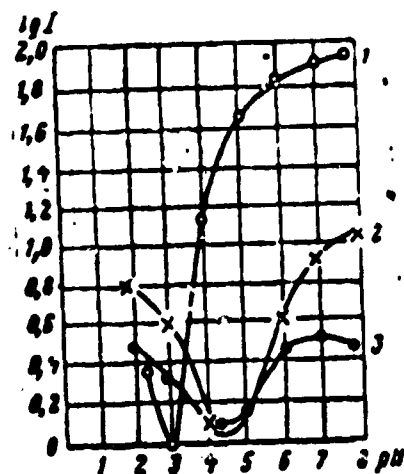


Fig. 211. Luminescence intensity of Porphyrines as a Function of the "pH" value:  
1 - Hematoporphrin; 2 - Isouroporphrin;  
3 - Uroporphrin.

Very close by its structure to the porphyrines is the chlorophyll (a complex salt of the porphin) which is the green pigments of the plants, and is biologically highly important. The chlorophyll absorbs the light energy, and transforms it into chemical energy of organic substances formed during the photosynthesis. The chlorophyll can exist in either of the two hard-to-be-separated modifications: the blue-green chlorophyll "A" ( $C_{55}H_{72}O_5N_4Mg$ ) and the bright-green chlorophyll "B" ( $C_{55}H_{70}O_6N_4Mg$ ). Usually, the leaves of plants contain three times as much chlorophyll "A" as chlorophyll "B". In organic solvents, the chlorophyll will produce an intensive, dark-red luminescence whose spectrum consists of two bands between 650 and 730 m $\mu$ . The bands of the chlorophyll "A" luminescence are somewhat shifted towards the long-waves as against those of the chlorophyll "B".

When performing a luminescence analysis of chlorophyll, they use the method of chromatographing on paper (# 108). They are handy when separating the chlorophylls "A" and "B", and also when separating the chlorophyll from some other pigments (for example, the carotinoids). In this case, one of the following: the benzine, petroleum ether, or acetone, serve as a solvent.

Luminescence Analysis of Antibiotics. Known are methods of luminescence analysis of some of the antibiotics (aureomycin, terramycin, etc.). These compounds are luminescing only in an alkaline medium. Aureomycin produces the most intensive radiation

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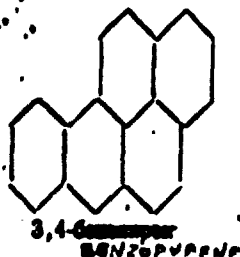
\* Antibiotics - compounds created by micro-organisms, which are capable to check or destroy bacterias or other microorganisms.

at pH ~ 8, the terramycin - at pH ~ 10. A necessary amount of caustic soda, and a little of butyl alcohol should be added to the biological liquid to be analyzed, or its extract; the caustic soda will raise the solution pH. The butyl alcohol will extract these substances from the solution. It has been ascertained that the intensity of the created luminescence varies with the concentration of the antibiotic in the solution, if the concentration is between  $5 \cdot 10^{-6}$  and  $5 \cdot 10^{-7}$  gram/milli-liter.

When an antibiotic is losing its biological activity, its luminescence spectrum will change considerably. For instance, the yellow-orange radiance of the aureomycin will turn into blue. The yellow luminescence of the terramycin will become greenish. Thus, by the spectral contents of their emission, the antibiotics can be checked as to their activity.

#### Luminescence Analysis of Cancerogenic Compounds.

In certain conditions, the cancerogenic substances can serve as exciters of the malignant cancerous tumors. Mostly, they represent polycyclical, aromatic hydrocarbons containing the cyclic groups of either phenanthrene or benzantracene; for example:



Many of them are contained in the by-products of coal.\*\*

The cancerogenic substances produce an intensive luminescence whose spectrum consists of three or four strips. It could not be ascertained if there is any direct link between their luminescing and cancerogenic properties. However, their intensive and characteristic radiance can be utilized for analytical purposes.

It is very hard to determine the cancerogenic substances, notably the 3,4 benzopyrene, in tars because their radiance is hindered by luminescence of the basic substance. Moreover, different admixtures usually can be found in tars, and they may extinguish the radiance of the cancerogenic compound. Therefore, the tars should be dissolved in vaseline oil where the strips of the benzopyrene become narrow and clear; also, due to the solvent high viscosity, the extinguishing properties

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\* Cancerogenic characteristics can be found also in other substances of a most varied chemical structure, for instance, the aminocompounds, and also some hormones.

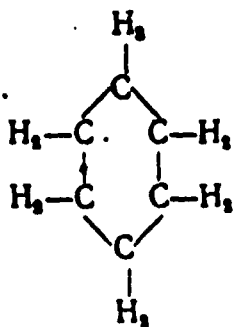
of the admixtures becomes less acute. For a better sensitivity of the analysis, the metering should be carried out at a temperature of liquid air ( $-180^{\circ}\text{C}$ ), when the luminescence strips become much more distinct. In this way, one can detect benzophenylene with a concentration of  $\sim 10^{-3}\%$  by the appearance of its most intensive line  $4035 \text{ \AA}$ .

At low temperatures, parallel to the fluorescence spectra, one can also use the spectra of phosphorescence which are considerably shifted towards the long waves. In this way, we can measure both spectra of radiance without using a phosphoroscope. In some cases, the spectra of phosphorescence are very characteristic, and they permit differentiating the isomeric cancerogenic compounds even though their fluorescence spectra fully coincide.

Even better results one can attain when performing the preliminary chromatographic fractionation of the sample, and placing it into frozen solutions of n-hexane or n-octane. If the sample contains the benzopyrene, the spectrum of its luminescence will become ruled, and the wave-lengths of its individual lines in these solvents will, with an accuracy of up to a decimal of one Angström, coincide with the lines of a pure Benzopyrene. In a similar way, one can detect cancerogenic hydrocarbons in the smoke discharges of factory stacks where benzopyrene reveals itself already at  $C \sim 10^{-9}$  gram/gram of substance.

#### Luminescence Analysis of Crude Oils and Bitumens

Bitumens are the gaseous, liquid or solid substances which consist of hydrocarbons or their derivatives. In nature, they can be found either in a pure form (tars, petroleum oils, natural gas), or in combination with various mineral rocks (oil shales, asphaltenes) or as organic solid formations (mined coal). Both the petroleum oils and other natural bitumens represent multi-component systems which consist mainly of various types of hydrocarbons. They include: the terminal paraffin hydrocarbons ( $\text{C}_n\text{H}_{2n+2}$ ), **NAPHTHENES** - aliphatic hydrocarbons of a terminal nature ( $\text{C}_n\text{H}_{2n}$ ) for example, the cyclohexane:



aromatic hydrocarbons (benzene and its higher homologs); non-terminal hydrocarbons ( $\text{C}_n\text{H}_{2n}$ ) of the ethylene ( $\text{H}_2\text{C} = \text{CH}_2$ ) order;

complex, high-molecular hydrocarbons; and some other substances.

Most of the above compounds produce a luminescence. The observable luminescence of petroleum oil represents a total radiance of all its numerous luminescing components. Consequently, the spectrum of luminescence will depend not just on the qualitative but also on the quantitative contents of the oil or bitumen. Many components cause the total spectrum to appear washed out and thus little fit for analysis. Another factor which significantly hampers the luminescence analysis of the petroleum oil, is the existence therein of large amounts of contaminating ingredients which either extinguish or conceal the radiance of its individual components. Various techniques have been worked out aiming at overcoming these obstacles. Particularly, it has been found advisable analyzing the narrow-temperature fractions of the petroleum oil, an parallel to their spectra of luminescence also to investigate their spectra of absorption.

At present, the luminescence analysis is being widely used for determination of both the qualitative and quantitative contents of bituminous substances in rocks, waters, clay solutions and in prospecting for oil fields. The high sensitivity of the luminescent method, and the convenience of an "instant" analysis, allow a fast prospecting of large areas in an oil-bearing territory.

One can apply any of the several types of the luminescence analysis: the method of a drop; that of a standard specimen; the method of a capillary; the method of components. In each of the above approaches, the excitation is being effected by either the ultra-violet or the short-wave, visible radiation.

The Method of a Drop consists in depositing a drop of luminescent solvent (usually the chloroform) on the surface of the ground rock sample. The chloroform dissolves the bitumen contained in the rock and, after having evaporated, it leaves a spot that will luminesce when subjected to an exciting light. By the shape of the spot and by the spectral composition of its emanation, one can determine the type and the approximate quantity of bitumen contained. Even with the equal amount of bitumen contained, but due to a varied friability of the rocks, the luminescing spots can have different shapes.

The Method of a Standard Specimen consists in dissolving a predetermined amount of the investigated sample in a known amount of chloroform. As a result, one obtains a solution of bitumen in chloroform with a certain, well known concentration. If the bitumen contents does not exceed  $10^{-3}\%$ , the radiance intensity will vary with the concentration. Therefore, before starting the analysis itself, one should carry out the "drop" method analysis which will establish the approximate contents of bitumen in the sample. Afterwards, a solution should be prepared with such a concentration that the rule of the proportion (intensity of radiance as a function of the concentration) is then determined by comparing the luminescence intensity of the

investigated solution with that of the standard one. Different types of the natural bitumen produce a radiance of a different spectral composition, consequently one should prepare several sets of the standard solutions made of various types of bitumen. This method turns out to be much more accurate than the described above method of a drop.

The Method of a Capillary presents a modification of a chromatographic analysis. A rock solution should be poured into a narrow glass or into a test tube, and one end of a strip of filter paper immersed into it for duration of 8-10 hours. Within this time, capillary infusions will appear on the strip in form of separate zones which will produce a luminescence when subjected to ultra-violet rays. By comparing the spectral composition, intensity and width of each of the luminescing zones of the investigated capillary infusions with those of the standard ones, one can determine the qualitative contents of the petroleum oils and bitumens in the sample. If a more detailed analysis is required, the above procedures should be performed in several solutions, in order of their dissolving capability (in alcohol-benzene, petroleum ether, caustic potash (2%), and others).

The Method of Components is based on procedures used in both the method of the standard specimen and that of the capillary, except applied to individual components of petroleum oils or bitumens (oils, tars, asphalts) which should be extracted from the sample by way of its successive dissolving in various solvents (for example, in the petroleum ether and in chloroform). Then, the radiance of the analyzed sample should be compared with standards i.e. either standard solutions or standard capillary infusions prepared for each component to be investigated, separately.

#### Special Procedures Used for a Quantitative Research on Luminescence of Petroleum Oils.

##### Exciting the Radiance by Waves of Different Length.

Both the petroleum oils and the bitumens represent a multi-component mixture of various luminescent substances. Therefore, to excite their radiance, it is advisable to apply individual spectral lines (for example, the lines of a mercury spectrum). When the wave-length of the exciting light is being varied, the luminescence spectrum of the petroleum will change, too, as will of the sample. This procedure will facilitate the determination of the qualitative and the quantitative composition of the petroleum oil.

##### Investigating the Spectra at a Low Temperature.

When carrying out an analysis of petroleum oils, it is recommended to investigate their spectra of fluorescence at low temperatures when the wide, washed-out bands appearing at a room temperature become narrow and sharp. Thus, they become easier to identify. In many cases, for instance in the kerosene fraction



of the petroleum oil, the luminescence spectrum is located in the near ultra-violet zone. Investigation of the luminescent ultra-violet spectra at a low temperature reveals that the radiance has been excited by the aromatic compounds.

When dissolving the sample in normal paraffins (n-hexane) at a low temperature. Quite often the spectrum of the luminescence becomes ruled. This fact permits determining the substance which excites the petroleum radiance. This was the way in which one had detected the existence of aromatic perylene hydrocarbons in the oil-bearing clays.

Research on the Spectra of Phosphorence. At the temperature of liquid nitrogen, different fractions of the petroleum develop not just the fluorescence but also the phosphorence. Here, in a B-process, the spectrum of radiance drastically differs from that of the fluorescence, and this feature can be used as an additional analytical characteristic. The above method gives good results when investigating the narrow, aromatic fractions of the petroleum oil.

Investigating the Polarization The Hungarian scientists have worked out a unique method of luminescence analysis of bitumens; the method is based on metering the polarization of radiance in solutions of rock specimens collected from the surface of the soil. Theory shows that the degree of the radiance polarization drops when the symmetry of molecules becomes higher (see # 110). The molecules of bitumen formed by organic substances in the surface layers of the soil, and the molecules of the oil-bearing bitumens have a different degree of symmetry. The former are less symmetrical than the latter. Thus, by the degree of polarization of the sample luminescence, one can evaluate the nature of bitumen contained therein.

#### # 113. Luminescence Analysis of Minerals and Ores.

The luminescence methods are being widely used in geological prospecting, in the mining industry, in controlling the concentration products of ores containing minerals, etc.

Ores and minerals are non-organic compounds, and the procedures described in # 111 can be applied to them. On the other hand, the luminescence analysis of these very important substances has a number of specific features. Many minerals represent crystallophosphors of a natural origin, whose characteristics of luminescence depends on the upsetting of periodicity of their crystal lattice. These disturbances will occur when activating admixtures are being introduced into the basic substance of the mineral - ions of heavy metals (rare-earth elements, Mn, Cr, Ag, S, [UO<sub>2</sub>]<sup>++</sup>, and others). Minerals will produce a radiance when excited by ultra-violet and X-ray radiation, and also under cathode rays. The most universal of them is the cathode excitation. A great majority of luminescent minerals can be excited to radiance in this way. The photo-excitation is less often applied; the X-rays are exciting only a limited number of minerals.

In order to apply the luminescence analysis to the non-luminescent minerals, the latter's grains should be subjected to chemical processing after which their surface will be covered by a film with its characteristic radiance. For instance, the mineral wolframite  $(\text{Fe, Mn}) \text{WO}_4$ , due to a special processing will be covered by a film of  $\text{CaWO}_4$  which will produce an intensive blue luminescence. There are worked methods of chemical processing for grains of the following minerals: Huebnerite  $\text{MnWO}_4$ , Beryl  $\text{Al}_2\text{Fe}_3[\text{Si}_6\text{O}_{18}]$  and Pollucite  $(\text{Cs, Na})[\text{AlSi}_2\text{O}_6] \cdot n\text{H}_2\text{O}$ .

To detect different metals in ores, and to determine their quantitative contents, they, too, should be subjected to a chemical processing prior to the analysis. In result of a luminescent reaction, new compounds are obtained which can produce a characteristic radiance; by measuring the latter's intensity, one can determine the contents of the given metal in the sample. These methods have been worked out for detection of such metals as: Li, Sn, Pb, Al and Zr in various minerals and ores.

When carrying out an analysis on ores and minerals containing uranium and rare-earth elements, one can use the techniques described in # 111. In case of the uranium, usually a pearl analysis should be performed, in case of rare earth elements one should apply a cathode excitation.

It should be pointed out that similar minerals mined in different fields, quite often show a different characteristic of their luminescence. This circumstance is due to their respective admixtures which can be different in different formations. Some of the ingredients (ions of Fe, Cu, Ni, etc.) are strong extinguishers of the mineral luminescence. These admixtures are called "Poisons" of the luminescence.

A qualitative luminescence analysis is being utilized when concentrating the ores which contain some minerals. Particularly often it is used when mining for the scheelite mineral  $(\text{CaWO}_4)$  which can produce a very intensive blue luminescence. During the concentrating process, a sector of the moving conveyor is being illuminated with ultra-violet rays, and the lumps which produce radiance are being taken aside.

The Roentgenoluminescence is applied when separating diamonds from rocks. Both the color and the intensity of the diamond luminescence allow a sufficiently accurate separation of the sample components. By the color of their radiance, the diamonds can be divided into three groups: one with a blue, the second with a green, and a third with a yellow luminescence. Within each group, there are possible more detailed sub-groups differing by the intensity of the excited radiance from one another. In the more complex cases the results of the luminescence analysis should be compared with the infra-red absorption spectra of the diamonds.

To control the products of ore concentration, they are applying both the semi-quantitative and quantitative methods of luminescence analysis, based on the use of cathode excitation. This technique gives good results in analysis on: scheelite  $(\text{CaWO}_4)$ ; willemite  $(\text{Zn}_2\text{SiO}_4)$ ; zircon  $(\text{ZrSiO}_4)$ ; spodumene  $(\text{LiAl}[\text{Si}_2\text{O}_6])$ ; apatite  $(\text{Ca}_{10}(\text{F, Cl})_2[\text{PO}_4]_6)$ , and other minerals.

In such a case, standard samples should be prepared which represent a mixture of the barren rock from the field in question, and a known amount of the mineral to be investigated. A collection of such samples is then placed into a vessel with radially partitioned sections. The investigated sample is placed into the center section. The vessel is then placed into a cathode cell, and the radiance of all samples is excited simultaneously. By comparing the luminescence intensity of all standard samples and the investigated one, we can determine the concentration of the investigated material in the sample. Accuracy of such an analysis does not exceed  $\pm 5\%$ .

Quite often, a qualitative luminescence analysis of ores and products of concentration consists of exciting the radiance of contained therein minerals, and of a statistical counting of their grains. Such a count gives a percentage of the mineral in the investigated sample. The analysis process itself can be divided into three stages: preparing the sample for analysis; preparing the compounds for analysis; counting the luminescing grains of the minerals.

Preparing the sample for analysis consists of preparing the batches consisting of grains of a similar size. For this purpose, the investigated sample should be ground and spread in a thin, several millimeter high layer. The layer is then divided into equal squares. A certain equal portion of the substance should be then taken off each square mixed together, and the final batch prepared. When working with non-luminescent minerals, the grain should be chemically processed so that a luminescent film will form on their surface.

The second stage consists of preparing the compounds for analysis. For this purpose, a square of certain size should be cut out from a graph paper, and pasted on a slide. On its other side, the glass shall be covered with a thin layer of glycerine, and then pressed against the smoothed surface of the investigated sample. In result, a mono-layer will form on the glass, consisting of grains of the investigated sample; here, the grains will stick only within the pasted square.

The analysis will be finished with counting the grains of the investigated mineral. For this purpose, the thus prepared compound is placed into a cathode cell where the radiance of the radiance of the luminescent components of the sample will be excited. A Binocular shall be placed above the cell window, the number of the luminescing grains can be then easily counted, and the percentage of the mineral determined.

As to its accuracy, the luminescence analysis of minerals equals the chemical analysis. However, it is much more simple, takes considerably less time, and thus gets the preference.

One should point out that the minerals, same as the crystal phosphori, are producing a characteristic, protracted after-radiance which fades away by a hyperbolic law (18.7). The fading-

away process, defined by the magnitude of the constant  $k$ , is very characteristic for a mineral. Thus, we can use in our analysis not just their spectral composition and the luminescence intensity of the minerals, but also the its process of fading away.

## CHAPTER 21

### The Luminescence Analysis of Detection

#### 114. Detection of the Invisible Radiance

A separate section of the luminescence analysis presents the detection of and the research on radiations invisible to the human eye - the infra-red, the ultra-violet and the X-ray, and also those formed during the radioactive disintegration and nuclear reactions.

Detection of the infra-red rays. As we know, a protracted radiance of the crystallophosphori is associated with a thermal liberation of the excited electrons from the localization levels. The illumination of the excited crystallophosphori by infra-red rays will, also, liberate the electrons from the levels of localization and speed up their fading. Two alternatives are possible here. In the first case, the liberated electrons perform emanating transitions which lead to an explosion of luminescence, in the second alternative, the electrons return to their non-excited state with no emanation, make the luminescence to fade; the latter phenomenon consists in darkening of those spots of the crystallophosphori surface where the radiation has been directed. Both of the above phenomena can be utilized for recording the infra-red rays.

The optical explosion can be observed particularly clearly in crystallophosphori with deep levels of localization from which, at a room temperature, the electrons cannot liberate themselves without any outside help. These excited, but not luminescing in the normal conditions, phosphori when subjected to infra-red rays, will produce a bright explosion. They are called the explosive phosphori. The explosive characteristics are proper to the alkali-earth crystallophosphori ( $\text{CaS}$ ,  $\text{SrS}$ , etc.) with two or more of the rare earth activators, for instance with  $\text{Ce}$  and  $\text{Sm}$  (green radiance) or with  $\text{Eu}$  and  $\text{Sm}$  (orange-colored radiance). The explosive phosphori permit detecting an infra-red radiation up to  $\lambda = 1.7 \mu$ . Crystallophosphori in which the infra-red rays would extinguish their luminescence, are called the fading-away phosphori. These properties are characteristic to, for example, the zinc-sulfide crystallophosphori activated by copper and cobalt ( $\text{ZnS} \cdot \text{Cu} \cdot \text{Co}$ ).

The detection of the infra-red rays is often performed by means of the, so called, "electronic-optical converters. In this case, one should need a luminescent screen sensitive to infra-red rays. However, with this method of investigation used, the screen's radiance will be excited not in result of a direct action of the investigated infra-red radiation, but due to electrons forced out of the apparatus photocathode by the infra-red rays.

The most simple electronic-optical converter consists of a vacuum discharge tube with a photocathode inside. The investigated flux of infra-red rays shall be projected on the photocathode from whose surface it will force out electrons. The latter are then sped up by means of electric field, and directed onto a luminescent screen which will start producing a visible radiance.

An image of different objects in the infra-red rays can be also projected onto the photocathode of an electronic-optical converter. Under the infra-red radiation, a visible image of the investigated object will appear on the luminescent screen.

Detection of the ultra-violet rays. The ultra-violet can excite most of the luminescent substances. When performing a qualitative observation of the ultra-violet radiation, they use mostly the uranyl glass in which it will excite an intensive, green luminescence. However, when transferring into the zone with  $\lambda < 300 \text{ m}\mu$ , the radiance intensity of this type of glass will drop markedly due to an acute absorption of short-wave portion of the ultra-violet spectrum by the glass itself. For quantitative metering, the uranyl glass is not fit enough as their absorption in the ultra-violet part of the spectrum is irregular. It is much more convenient to use the fused quartz glass which contains Ce. A cerium quartz produces an intensive, blue radiance formed when excited by light with  $\lambda$  from 380 down to 250  $\text{m}\mu$ , and has a sufficiently uniform absorption capability over the entire spectral range indicated above.

For recording the emanation located in the vacuum ultra-violet portion of the spectrum (with  $\lambda < 180 \text{ m}\mu$ ), the ordinary photographic materials are not suitable due to a high absorption of the radiation by the gelatine layer. The above difficulty can be overcome by covering the photo-emulsion by a thin layer of industrial oil; the latter's luminescence excited by the short-wave, ultra-violet emanation will blacken the photographic film.

Detection of X-rays. The X-ray radiation excites the luminescence of numerous crystallophosphori, different types of glass diamonds and other non-organic compounds. The radiance is being excited by fast electrons torn off the electronic shell of the atoms or molecules by the X-rays. The X-ray radiation can be registered either visually (the Roentgenoscopy) or on a photo film (the Roentgenography). For the use in Roentgenoscopy, they manufacture luminescent Roentgen screens consisting of a thin layer ( $\sim 0.2 - 0.4 \text{ mm}$ ) of powdered crystallophosphori applied to either a cardboard or plastic padding by means of a transparent glue. Radiance of such screens should be inertia-free so that one could clearly see the outlines of a moving object, for instance, those of a pulsating heart. To obtain a clear image of minute details of the object, the screen should be highly discriminating, a feature which can be attained by using a finely ground powder.

The Roentgen screens used in the Roentgenoscopy are made of crystallophosphori which produce either yellow-green or green radiance, to both of which the human eye is most sensitive. Usually they are made of either zinc sulfide ( $\text{ZnS}$ ) or phosphori mixed with base -  $\text{ZnS-CuS}$ . They use Ag as an activator.

The Roentgen screens used in Roentgenography for amplification of the photographic action of X-rays, are being made of  $\text{CaWO}_4$ ,  $\text{MgWO}_4$  or  $\text{ZnS-Ag}$ . They produce a blue or a blue-violet radiance. When superimposed on a photo-film, the amplifying screens should be excited by X-rays; their radiance will affect the photo-emulsion several times stronger than a direct illumination. Thus, the duration of the exposure can be drastically reduced.

Detection of elementary particles and  $\gamma$ -rays. By way of luminescence, one can register the flows of protons, deuterons, electrons, neutrons, positrons, mesons,  $\alpha$ -particles and  $\gamma$ -rays. When any of the above particles is passive through a luminescent organic or non-organic substance, it will excite a great number of their radiance centers whose emanation will produce a flash of luminescence called the "scintillation." For example, a single  $\alpha$ -particle can excite  $\sim 10^6$  centers of radiance. The luminescent substances with the above characteristics, are called the "scintillators." The scintillation can be detected and measured by using a scintillation counter which consists of a scintillator and a photo-amplifier recording the individual light impulses.

Similarly to the Röntgenoluminescence, a radioluminescence is being excited by secondary electrons which formed due to particles hitting a scintillator.

The scintillators can consist of some crystallophosphori, organic mono-crystals, solutions of organic substances, or of special types of plastic.

The most widespread non-organic scintillators are the zinc-sulfide crystallophosphori activated by either copper ( $\text{ZnS}\cdot\text{Cu}$ ,  $\lambda_{\text{max}} = 520 \text{ m}\mu$ ) or silver ( $\text{ZnS}\cdot\text{Ag}$ ,  $\lambda_{\text{max}} = 450 \text{ m}\mu$ ). When the excitation is by  $\alpha$ -rays or other highly ionizing particles, the energy output of their radiance can go up to 25%. However, due to their high dissipation, such pulverized scintillators are not too effective for registration of  $\gamma$ -rays. Moreover, they produce a considerable after-radiance ( $\tau > 10^{-5} \text{ sec.}$ ), and thus hampers the measuring of the individual scintillations.

For detection of slow neutrons, they are using a mixture of  $\text{ZnS}\cdot\text{Ag}$  with  $\text{B}_2\text{O}_3$ , where the neutrons are being trapped by the boron, and  $\alpha$ -particles are being separated which will excite the radiance of  $\text{ZnS}\cdot\text{Ag}$ . When metering the flow of fast neutrons, good results are being obtained by using a mixture of  $\text{ZnS}$  and polystyrene. For registering the  $\gamma$ -rays, one can use the transparent alkali-haloid mono-crystals ( $\text{NaI}$ ,  $\text{KI}$ ,  $\text{LiI}$ ,  $\text{CsI}$ ) activated by  $\text{Tl}$ . Most of these crystals are hygroscopic; to protect them from moisture they should be covered with a film of light oil. The  $\gamma$ -scintillators can also consist of  $\text{KI}\cdot\text{Tl}$  powder mixed with  $\alpha$ -bromonaphthalene, or crystals of calcium tungstate ( $\text{CaWO}_4$ ) and cadmium tungstate ( $\text{CdWO}_4$ ). Monocrystals  $\text{NaI}\cdot\text{Tl}$  are being used for registration of protons and deuterons. Table 39 shows the characteristics of some non-organic scintillators.

Dosimetric metering of  $\gamma$ -emission can be carried out also by observing the thermoluminescence brightness (96) of some of the crystals (for example,  $\text{LiF}$ ); in identical conditions of experimenting, the thermoluminescence is proportional to the number of  $\gamma$ -rays absorbed. The above method is being used for medical purposes, in determining the intensity of the internal emanation in cancer-sick people treated with radioactive isotopes. Small, water-insoluble crystals of  $\text{LiF}$  were swallowed by the patient, and then retrieved after two days. The intensity of their thermoluminescence was being

compared with that of the crystal which has been previously exposed to a predetermined dose of X-rays; by comparison, one can determine the dose, in Roentgens, to which the patient has been exposed.

Table 39

① Основные характеристики некоторых неорганических сцинтилляторов

② Фосфор	Средняя длина волны спектра излучения, мμ	Энергетический выход, %	Время затухания, сек.
③	④	⑤	⑥
NaI·Ti	410	8	$2,5 \cdot 10^{-7}$
KI·Ti	410	2	$> 10^{-6}$
LiI·Ti	синие-зеленый — ⑦	1	$> 10^{-6}$
CaI·Ti	белый — ⑦	6	$> 10^{-6}$
CaF	слабый, ультрафиолетовый — ⑧	0,3	$5 \cdot 10^{-2}$
CaWO <sub>4</sub>	430	$> 5$	$\sim 0,5 \cdot 10^{-6}$
CdWO <sub>4</sub>	530	$\sim 10$	$\sim 0,5 \cdot 10^{-6}$

- 1- Basic characteristics of some non-organic scintillators
- 2- Phosphorus
- 3- Average wave-length of the emission spectrum, in mμ
- 4- Output of energy, in %
- 5- Time of fading out, in sec.
- 6- Blue-green
- 7- White
- 8- Blue, ultra-violet

Also, known is the method of dosimetry of the  $\gamma$ -emanation, based on the utilization of exploding phosphors SrS·Eu·Sm which, when subjected to the infra-red radiation, will produce a bright flash of radiance. In this case, the phosphors should be preliminarily excited by the investigated flux of  $\gamma$ -rays, and then exposed to infra-red rays. The brightness of the thus created flash will permit evaluating the dose of the  $\gamma$ -radiation.

The above method allows measuring the intensity of the  $\gamma$ -radiation in a very wide range. From 0.005 up to 1,000 roentgens. A similar technique can be applied to metering the intensity of the  $\beta$ -radiation, as well as the flow of the slow neutrons.


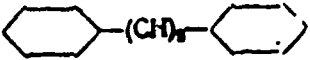

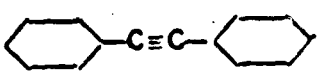

When registering the elementary particles and  $\gamma$ -rays, one can use the monocrystals of anthracene, stilbene, terphenyl, toluene, naphthalene and some other organic substances. The above crystals provide a wide resolving capability in time, as the duration of their scintillation is  $\sim 10^{-8}$  sec. Their shortcoming consists of a lack of proportion between the



radiance intensity and the energy of hitting particles. Table 40 shows the characteristics of some of the organic scintillators.

Table 40

①- Основные характеристики некоторых органических сцинтилляторов

Вещество ②	Структурная формула ③	Средняя длина волны спектра излучения, мμ ④	Энергетический выход, % ⑤	Время затухания, сек ⑥
⑦- Антрацен		447	4	$\sim 3 \cdot 10^{-8}$
⑧- Стильбен		410	$\sim 2$	$\sim 7 \cdot 10^{-9}$
⑨- Терфенил		415	$> 2$	$\sim 10^{-8}$
⑩- Толан		390	$> 2$	$\sim 7 \cdot 10^{-9}$
⑪- Нафталин		345	1	$\sim 7 \cdot 10^{-9}$

- 1- Main characteristics of some of the organic scintillators
- 2- Name of substance
- 3- Structural formula
- 4- Average wave-length of the emission spectrum, mμ
- 5- Output of energy, in %
- 6- Time of fading out, in sec.
- 7- Anthracene
- 8- Stilbene
- 9- Terphenyl
- 10- Tolane
- 11- Naphthalene

The part of scintillators can be played also by the solutions of some organic substances (paraterphenyl, 2.5 - diphenyloxazole, phenyl - α - naphthylamine, etc.) with a concentration of  $\sim 5$  gram/liter. Xylene, phenycyclohexane, toluene, benzene and some other organic substances can serve as solvents. Sometimes, into such a solution they are adding a small amount of a second organic substance whose spectrum of luminescence is shifted toward the long waves, as against the spectrum of the main substance. These

admixtures are called the "spectrum displacers." In the above system, a resonance transfer of the excitation energy proceeds from the solvent, through the dissolved substance, to the admixture whose radiance will be registered. In this way, one can shift the spectrum of scintillation into the zone of a maximum sensitivity of the photo-amplifier used for the registration.

For registration of nuclear radiations, they use also plastic scintillators into which they have introduced some luminescent organic substance (paraterphenyl, 2.5 - diphenyloxazole, and many others). In the plastic scintillators, the part of spectrum displacers is being played usually by the quaterphenyl, tetraphenybutadiene, and other substances. In their characteristics, the plastic scintillators resemble other organic scintillators.

#### 115. The Luminescence Analysis of Detection as Applied in Biology and Medicine

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As mentioned above, the chemical analysis of luminescence is being widely used for determination of vitamins, hormones, pigments and other important biological substances. Equally widespread in both biology and medicine, are the methods of the luminescence analysis of detection.

Luminescent Microscopy. At present, of particular importance are the luminescent-microscopic investigations concerning either the natural radiance of analyzed object or the radiance of a sample which has been preliminarily colored with dyes called the "fluorochromes." The latter can be: the xanthene, thiazine, quinoline and acridine dyestuffs, some luminescent pigments (chlorophyll, porphyrin), and a number of organic compounds.

The natural radiance is being utilized for the luminescent-microscopic research on vitamins A, B<sub>2</sub>, B<sub>6</sub>, some derivatives of vitamin B<sub>1</sub>, nicotine acid and a number of other compounds. Here, one can follow the precipitation of these substances in various organs or in individual cells, and also one can observe their transformations during the active life of the organism.

The use of the fluorochroming method considerably widened the possibilities of the luminescent microscopy. Now, concrete images can be obtained, and even the smallest details of the investigated object can be investigated regardless of its natural luminescent properties. Of particular importance is the circumstance that some dyes, while being adsorbed by tissues, cells and their various parts in a different manner, when subjected to exciting beams, will produce a very contrasting, multi-colored picture.

For instance, after a cell has been colored with aurophosphine, the protoplasm will produce a dark-green radiance, the nuclei-light green, the chondriosomes - orange, and the fatty matter - blue.

On the other hand, after having been fluorochromed with acridine, orange dye, the dead cells will produce a bright-red luminescence, the live ones - a bright green. Thus, they can be easily discerned from each other.

A similar method is being used in diagnostics on cancer. In this case, the radiance of fluorochrome allows a faultless distinguishing of the healthy cells from those affected by cancer.

The Method of Fluorochroming the Live Organisms. Considering the extremely high sensitivity of the luminescent method for the purpose of coloring they are using highly diluted solutions of the fluorochromes ( $C \sim 10^{-5} - 5 \cdot 10^{-6}$  moles/liter) which can only slightly affect chemically the investigated object notably the organism cells. Thus, by either the intravenous or subcutaneous injection one can fluorochrome the individual organs of human beings and animals while they are alive, an achievement which is extremely important for the biological research. By using the above method, one can study the structure of cells, and follow their changes during various functional conditions of the organism. For instance, by fluorochroming the live cells with the acridine orange dye ( $C \sim 1:1 \cdot 10^5$ ) one can observe the conditions of cells of the brain cortex of various creatures, thus detecting the finest structural elements of the brain tissue.

A technique has been worked out for making micro-motion pictures of the fluorochromed, simplest living organisms. These pictures turn out to be essential when studying the biological influence on organisms of the ionizing emanation.

By means of the fluorochroming one can follow the relocation and transformation of various substances in members, tissues and cells of a living organism. When carrying out a research on a living body of animals, the fluorochrome is either applied to the bare surface of the member, or injected. The blood stream carries the fluorochrome over the entire body, and when illuminated with ultra-violet rays, the substance will luminesce brightly coloring spots of the skin and mucuous membrane. The fluorochroming method is also being used in the research on circulation of blood and other liquids in the body.

The Luminescence Method of Diagnosing Various Diseases. For the purpose of diagnostics, one can, by using the fluorochroming, detect various bacteria. For instance, by using the auramine dyes or the acridine yellow, one can detect the bacillus of tuberculosis; the coryphosphine permits watching the bacillus of diphtheria; berberine sulfate- the bacteria of leprosy; rivanol successfully reveals the plasmodia of malaria and some spirochaeta. Minute numbers of bacteria can be detected by means of the pseudoisocyaninchloride which, though not producing a natural luminescence when in solutions, becomes adsorbed on the bacteria surface. After having been treated with fluorochromes, the luminescence of related bacteria may turn out to be similar. In order to distinguish one from another, they use the extinguishers of luminescence; in this way, one can either weaken or fully extinguish the radiance of one type of bacteria, while the other goes on producing an unchanged luminescence.

The luminescence analysis can be used for determination of existence of the cancerogenous substances, and thus to take the suitable steps in order to protect the human life. For the purpose of diagnostics, the

patients receive intravenously the fluorescein. In a healthy man, the latter starts separating in 50 - 70 hours. When a malignant swelling is existing, this time will increase to 2,000 hours. There are also known methods which allow to diagnose the cancerous swellings directly on the operation table. Here, they either watch the natural luminescence of the affected organs, or fluorochrome them with a fluorescein dye. By their specific radiance, one can establish the outlines of swelling spread and thus determine the location of the metastasis. This method requires a highly intensive ultra-violet light for the excitation purpose; it can be obtained from a special floodlight equipped with lamp, type SVDSH-250, and screened with the UFS-4 filter. By this method one can determine a hard-to-be-detected cancer of pleura, and also distinguish various types of skin cancer.

The luminescence methods represent a great aid to the surgeon also in other types of operation. For example, when operating on the brain tumor, by using the fluorescein one can distinguish the normal tissues from those tumorous, and also establish if they are malignant or benign. During transplantation of skin, a fluorescein solution should be introduced into the patient's blood; in this way, one can determine the extent to which the transplanted tissue has taken root, and if a normal blood circulation is being maintained therein.

The luminescent analysis of detection is widely used for controlling the quality of various drugs, and for research on their usefulness. It is also used in dermatology. When subjecting the affected skin areas to ultra-violet rays, one can immediately establish the type of disease and the outlines of its spread. For instance, by fluorochroming with an acridine orange dye, one can reliably distinguish different types of the skin cancer and sarcoma. Equally important are the luminescence methods for the pathological anatomy and in the criminology.

#### 116. The Luminescence Analysis of Detection as Applied in Industry

##### Detection of Defects by Luminescence

In various branches of industry, the methods of the defect detection by luminescence became widespread; they permit detecting the minutest cracks and defects on the surface of industrial products. The superiority of the luminescence method over the others consists of its versatility; the luminescence methods can be applied to parts made of any material, or of any shape and size, regardless of the type and quality of the surface machining.

There exist several methods of defect detection by luminescence. The most widespread of them consists of the following procedures. The part to be investigated should be first washed in benzine in order to remove any grease from its surface. Any slag should be removed by sanding. After the part has been dried, its surface should be covered by a luminescent mixture (for example, a solution consisting of kerosene, benzine, transformer oil and a dye of green-golden defectole) which within a short time (~10-15 min.) will penetrate into all pores and defects of the surface.

Next, the mixture should be washed away by a water stream for 5 - 10 seconds. The part dried out by a stream of hot air, its surface sprinkled with a desiccated, thoroughly ground silica gel ( $\text{SiO}_2$ ) which will absorb the solution which got into the cracks, and bind with the surface tightly. Then the silica gel should be removed by shaking the part, and blowing; it will stay only inside the cracks where it remains moist. When the object is then illuminated with ultra-violet rays, the luminescing zones around the cracks will be distinctly visible on the dark background.

The above technique allows detecting cracks up to  $1\mu$  deep. The observation is quite easy as the luminescing strip is usually about 10 times wider than the crack itself. It has been ascertained by Karyakin, that the silica gel will not start radiating immediately but after a certain delay called the "detection period." The detection period depends on the depth "h" of the crack, and varies from 30 seconds (deep cracks) up to 30 minutes (small cracks,  $\sim 1\mu$  deep). By measuring the time "t" until the luminescent strip will become visible, and the strip width l, from the curves (figure 212, a and b) one can quite accurately determine the depth h and the nature of the crack on the surface of the investigated part.

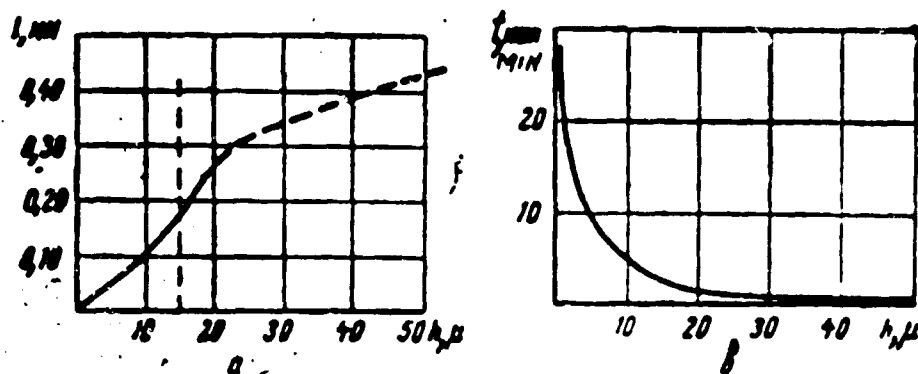


Figure 212. a- Width l of the fluorescing strip as a function of the crack depth h;  
b- Detection period t as a function of the crack depth h.



Figure 213. Picture of detail with cracks invisible to human eye detected by luminescence.

Figure 213 shows a part on whose surface, by means of luminescence, were detected cracks invisible to a human eye.

In a similar way, one can detect through cracks in pipes and other tubular surfaces. For this purpose, their inner surface should be covered with a luminescent composition. After having subjected their outer surface to ultra-violet rays, on the dark background of the detail, all the through cracks and defects will be distinctly visible.

Another method of detection is applicable only to products made of material with magnetic properties (steel, cast iron). This method is modification of that of the defect detection where pulverized magnet is being used. The part to be investigated should be covered with a magnetic suspension consisting of crocus and a luminescent mineral oil. A magnetic field should be induced in the part. After the electric current has been cut, the most intensive residual magnetic fields will form on the surface defects. As a result, the luminescent magnetic suspension will settle along the crack edges, and will become visible when illuminated with ultra-violet rays.

Detection of defects by luminescence plays an important role in the radio-manufacturing industry when mass controlling the vacuum devices for leakage. For this purpose, they are using substances (for example, lumogen orange-red II in trichloroethylene) with an intensive red or orange-red luminescence whose color will exclude the chance of false alarm considering that the glass itself, or its chance ingredients, produce a more short-wave radiance. A degreased and cleansed specimen should be immersed into a luminescent solution which due to capillary forces will, through the leaks, penetrate into the device. Next, the solution should be washed away from the device surface with pure trichloroethylene, and the device illuminated with ultra-violet rays. The radiance of the luminophore which remained on the inner surface of the device will indicate the leaking place. By holding the specimen in the solution for longer time, we can detect also the smaller leaks (Table 41).

Table 41

Magnitude of the detected leak as a function of the holding time of specimen in solution

Holding time	Minimum size of the detected leakage (in mm. of mercury column. $\text{cm}^3/\text{sec.}$ )
Minutes	$\sim 10^{-3}$
Hours	$\sim 10^{-4} - 10^{-5}$
Several days	$\sim 10^{-6} - 10^{-7}$

When investigating the products made of clay, ceramics, concrete, etc., they are making use of the difference of liquid adsorption to a smooth porous surface and that with cracks. The particles suspended in the solution, into which the product is being immersed, are usually much bigger than the material's pores. When the material absorbs the liquid, the luminescent particles will concentrate in the crack and settle along its edges. Their radiance will reveal the defects in the product surface. The above method is being widely used as a quality control of the high-voltage insulators.

There are known also other variations of the defect detection by luminescence. Each of them leads to a drastic reduction of faults, and raises the quality of the manufactured products. This kind of defect detection is particularly important for the manufacture of steam turbines, aviation and reactive motors, where even an insignificant crack or defect on the surface can cause a serious break-down when in operation. In workshops, special luminescence defect detectors do the job.

#### Other Types of Luminescence Analysis of Detection

The luminescence analysis has found various applications in the industry. The luminescence analysis of detection is being widely used in the manufacturing of optical-mechanical apparatus where it is for marking various types of processed glass.

The radiance of glass is being excited by short-wave ultra-violet rays ( $\sim 300 - 250 \text{ m}\mu$ ) generated by electric spark. The objective of observation is the momentary radiance of the glass ( $\tau \sim 10^{-5} \text{ sec.}$ ), as well as its phosphorescence ( $\tau \sim 10^{-2} \text{ sec.}$ ) separated by a phosphoroscope. The radiance of the investigated specimens is then compared with that of a set of standards. In this way, one can fast distinguish over 40 types of the optical glass.

With certain modifications, the above method can be applied to analysis on the composition of emery where the contents of corundum is being determined by counting under a microscope its bright luminescing grains easily discernible from those of the other components.

The luminescence analysis of detection is being used also in the rubber industry. The production of rubber objects consists of preparation of a rubber mixture, and its subsequent vulcanization. The rubber mixture consists of caoutchouc and different chemicals which impart to the rubber product the porosity, elasticity, flexibility, water-resistance, acid-resistance, etc. During the vulcanization, the rubber mixture is being heated together with the vulcanizing substances (for instance, the sulfur). One can add to the mixture also the vulcanization accelerants, and also some substance which will protect the rubber from an early deterioration. All the components should enter the mixture in a rigidly maintained proportion if the required properties of the finished product are to be as expected.

Most of the rubber components can produce luminescence, and this feature is being used for control of the entire process and its individual stages, and also the check-up on the finished products. For example, by the color of their respective radiance, the rubber mixtures can be sorted, the existence or lack of a sufficient amount of the vulcanization accelerants determined, a natural or artificial deterioration of rubber-controlled, etc.

In the textile industry, the luminescence analysis is being used for controlling the quality of colored designs printed on fabrics. Brightly luminescent dyes (fluorescein and betanaphthol) are being introduced into the coloring mixtures, and the fabrics are being looked over in ultra-violet rays directly while being printed. In this way, one can continuously control the quality of the obtained design, and considerably reduce the number of rejects. By using the luminescence, one can control the dyes, detect greasy spots on fabrics, etc.

The luminescence analysis of detection is also used in the pulp and paper industry. The intensity and color of the radiance indicates the extent of decay in the technical cellulose, allows distinguishing the bleached pulp from the unbleached one, young timber from the old one, etc. Moreover, one can determine the moisture - and oil-resistance of the paper by watching under an ultra-violet light how it absorbs the luminescing, water-diluted solutions, mineral oils or fats colored with luminescent pigments.

The luminescence analysis of detection is being used also in other branches of industry. For example, in the chemical industry it controls the quality of liquid oxygen and detects lubricating oils which got into it from compressors during the air-liquefying process; likewise, the luminescence analysis of detection controls the allowable contents of oil products in water in steam boilers, a factor which affects their correct operation. By observing the radiance on the edges of the insulating hose rubber, from the speed and penetration depth of the oil or crude oil, one can evaluate its resistance to both. The luminescence analysis of detection is also very helpful in the diamond mining industry where a characteristic radiance excited with X-rays, allows an easy separation of diamonds from other minerals and rocks.

#### 117. The Luminescence Analysis of Detection as Applied in Agriculture and Foodstuff Industry

The Luminescence Analysis of Food Products. The luminescence analysis of detection is being used for sorting food products, seeds, vegetables, etc.

By the color of their luminescence one can detect when the food products start rotting long before it becomes visible under the ordinary light. Such preliminary sorting allows a protracted storage of products, and is also useful in the manufacture of canned food. The methods applied here are simple and easy. The product to be analyzed is simply illuminated with



either ultra-violet or short-wave visible rays. In southern parts of the country, the sun rays are used for exciting the radiance. In that case, the products should be placed in the sun luminoscopes (see 105). In this way, one can detect the early stage of rotting in cucumbers, beans, cabbage, potatoes, oranges, mandarins, and other vegetables and fruits. Moreover, healthy vegetables can be distinguished from those affected by fungus, mold, eurygaster or frost. For instance, fresh mandarins produce a dark orange luminescence; those affected by mold invisible to the human eye will luminesce in the affected spots with a blue light.

Also the quality of other food products can be controlled by means of their luminescence. For example, the flour grade can be established by the color of its radiance. The more bran it contains, the more intensive its radiance which will turn from light blue into dark blue. Ergot can be easily detected in the flour by its yellow-orange luminescence. By using the ultra-violet rays, one can also control milk, eggs, egg powder, fish, etc.

Determining the Germinating Power of Seeds. Using the luminescence analysis, one can by elimination, establish the seed germinating power of various agricultural crops as well as species of tree. It turned out that the radiance color of seeds of oats, wheat, barley, corn, flax, fir, pine, cedar, etc., depends, to a great extent on their germinating power. For a better contrast, the cross-sections of the germs can be colored by various fluorochromes. For example, the barley germ is being colored with a 1% soda solution of the rhodamine 6ZHDN dye. The germinating seeds of barley produce a bright yellow radiance, the germs of wheat-yellow. In either case, the seeds incapable of germinating produce a dull-brown luminescence.

Another technique is based on the use of fluorochromes - indicators which change their radiance when changing the magnitude of their pH; this change occurs always in the germs of different germinating power. For instance, the germs of barley and wheat should be colored with a water-alcohol solution of dimethylnaphthorhodine ( $C = 1 \cdot 10^{-3}$  gram/milliliter). After the above treatment, under an ultra-violet light, the germinating seeds will produce a bright, light-yellow radiance, the non-germinating ones - a dull, pink-orange luminescence. Similar methods permit determining the germination of seeds of the corn, flax and oats.

Particularly important is the luminescence analysis in the control on the tubers of potato which, after they have been stored for certain periods, are being used for planting. Here, one can determine various diseases of the potato, as well as detect the frozen tubers; the frost-bitten spots produce a whitish-blue radiance easily discernible on the background of the yellow or gray-brown luminescence of a healthy tuber.

#### 118. Detection of the Hidden Currents

Investigating the Water Current. An extremely high sensitivity of the luminescence methods facilitates the detection of a subterranean link between rivers and water reservoirs. For this purpose, some tens of liters of concentrated solution of any brightly luminescing dye (for instance, the fluorescein) should be dropped into one of the water reservoirs; at certain

intervals; from another reservoir, samples of water are being taken for analysis. Provided the two reservoirs are interconnected, the samples will reveal the presence of the luminescent dye. The above method has been used to prove a link between the two biggest European water systems: that of the rivers Rhine and Danube. The coloring of the water with luminescent dyes, is also used in the research on water currents in the existing models of hydrotechnical installations.

Investigating the Air Currents. The luminescent substances are being used for investigating the characteristics of air currents existing along the wind tunnels. For example, when studying the distribution of pressures in a wind tunnel, at pressures  $\sim 50-20\mu$  of mercury column, observation is being carried out on the after-radiance of gases (air, argon or helium) which have been preliminarily excited with a high-frequency discharge. When the gas travels from the discharge into the wind tunnel, the distribution of its density becomes clearly discernible in the supersonic shock wave.

Investigating the Transfer of Substances in Biological Objects and in Plants. Similar methods are being used in the biological research and in the study on physiology of plants. In the former case, solutions of harmless dyes (fluorescein) are introduced into the blood stream of an animal or human being, and then one can watch how a substance is traveling in the organism. In the ultra-violet light, right through the skin, one can see the spread of the fluorescein. After the fluorescein has been injected intravenously, and after a certain time necessary for blood circulation, individual organs (eyelids, lips, tongue) will adopt a greenish-yellow color. Thus, one can determine the blood circulation time of healthy people and those with heart condition. In diseases affecting the peripheric vascular system, no radiance appears in the places with the weakened blood circulation. This feature is being used in diagnostics concerning an upset blood circulation.

Similar techniques are being applied for investigating the transfer of substances in living plants. The dye used for coloring should produce a luminescence drastically different than that of the plant tissues. Usually, they take either fluorescein or esculin which produce an intensive green or blue radiance, respectively. The dyes are being introduced into the plant in form of a water or gelatine solution. In an ultra-violet light, one can see the speed and the direction of the spreading solution.

The Method of Marked Sands. The national economy is suffering a great harm from elemental relocations of huge masses of sand both on the land and under water. This disaster can drift over various land installations, washes away and knocks down the coast, forms shoals and sandbanks on navigational routes, etc. In order to fight the above disaster, and also when building dams, harbors, hydropower stations, etc., it is necessary to anticipate the relocation of sand masses for a long period ahead.

These forecasts can be composed by using the method of marked sands, worked out by Matveev. The grains of natural sand should be coated with a

thin layer of transparent material containing a brightly luminescent substance. From several kilograms up to several tons of the marked sand are introduced into the sand mass. After a certain time has passed, at various distances from the place the marked sand has been dumped, samples of soil should be taken and exposed to an ultra-violet light. In this way, marked sand grains can be detected in the soil, even if they are strongly diluted as, for instance,  $\sim 1:10^7$ . By counting the number of the luminescing grains, we can determine the relative amount of the marked sand in the sample. Thus, we can determine the direction, width of the front, the zone of the maximum intensity, speed and distance covered by the relocated natural sand.

If the sample contains a high percentage of the marked sand, it will become hard to count the luminescing grains. Here, the analysis should be carried out in a different way. The sand should be colored with fluorescein, 2,2' - hydroxyphenyl benzoxazole or other luminescent substance which through non-water soluble, will form brightly luminescent liquids in the alkaline water solutions. Each sample of soil should be washed with water so that all soluble ingredients are removed, and then treated with 1% solution of caustic soda. The soil will then be filtered and again washed in water; next, the radiance intensity of the filtrate should be compared with that of the standard solutions containing a known concentration of the same luminescent substances. By using the above method, one can detect the marked sand when diluted in the sample in proportion of  $\sim 1:10^5$ .

#### 119. Luminescence Analysis of Detection as Applied to Paleontology, Archeology and Criminology

The luminescence analysis of detection is very helpful in the paleontological, archeological and criminological research. Being highly sensitive, simple, and fast, it becomes irreplaceable in such investigations. Another important feature is that in the process of analysis, the investigated object is not subjected to any destruction or modification, and remains in its original form after the analysis has been terminated.

The Luminescence Analysis of Detection in Paleontology. Here, the luminescence analysis is used for investigation on imprints of ancient animals and plants in the sedimentary rock. In daylight, these imprints seem to be washed out. When illuminated with ultra-violet light, the imprints start luminescing, and thus one can see the structural details of the prehistoric animals and plants.

The Luminescence Analysis of Detection in Archeology. In archeological investigations, the luminescence allows the determination of worn-out, faded or eroded spots in ancient manuscripts and documents. Usually, it is sufficient to illuminate the affected areas with ultra-violet rays. However, if the letters have been written in ink containing aniline dyes (methylene violet, methylene blue), the above method does not produce a satisfactory result. Then, the infra-red luminescence of the document should be excited by the visible rays of a powerful incandescent lamp, and a picture of the document taken.



Figure 214. a- photo of a forged document in a visible (top) and ultra-violet (bottom) light  
b- photo of a letter written with invisible ink, under ultra-violet light.

GRAPHIC NOT REPRODUCIBLE

In this way, one can restore the text which became invisible in ordinary conditions due to fading of the dye contained in the ink. The above method will also reveal the faded areas of a typewritten text. By using the luminescence, one can also detect the early stages of the paper being affected with fungus. Luminescence is being applied in laboratories for protecting or restoring various documents.

The Luminescence Analysis of Detection in Criminology. Particularly important is the luminescence analysis for criminology, forensic chemistry and forensic medicine. It is being widely used in the court practice where it unmistakably detects various forgeries, erasures and other traces of foul play. These methods are based on illumination of the objects with ultra-violet rays, and watching their radiance. As a rule, each substance produces its own characteristic luminescence. For example, it is almost impossible to find two types of paper which would produce a similar radiance. In this way, one can establish the authenticity of valuable documents, notes, shares, etc. The minutest tampering becomes visible to a naked eye. Particularly distinct, are the marks on a water-lined paper. Figure 214 serves as an illustration. The forgery of the date is clearly visible in the picture.

In a similar way, one can detect also other types of forgery. As we know, the surface of marble, bone, glass and other materials, after it has been exposed to air for a long time, starts producing a characteristic luminescence which only slightly resembles the radiance of recently manufactured objects. In this way, one separates the authentic art objects from forgeries of a more recent origin. Similarly, one can detect the traces of tampering with old paintings, invisible in a daylight but easily recognizable in the ultra-violet rays. Thus, one can verify the original signature of the painter, and also study the history of the painting by observing the radiance of paints applied after the work has been finished.

The luminescence analysis can reveal the text of a letter written with the ink invisible under ordinary conditions. Figure 214 b, shows a picture of such a letter whose text is clearly visible under the ultra-violet light (white letters on a dark background). One can also restore manuscripts over which ink has been spilled. Here, the text should be covered with a special luminescent compound, and then illuminated with an ultra-violet light—dark letters of the overspilled area will appear on a brightly luminescent background.

By using luminescence, one can detect various spots on fabric, clothing and other objects. In this way one can detect spots of blood, saliva, perspiration, urine, grease, etc. The grease on fingers produce very clear luminescent fingerprints. The luminescence analysis can detect traces of the gun oil around the bullet hole, compare different fabric threads, and perform many other investigations associated with criminology.